

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Cobalt has been identified in at least 404 of the 1,585 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2001). ^{60}Co has been identified in at least 11 of the 1,585 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2001). However, the number of sites evaluated for cobalt and ^{60}Co is not known. The frequency of these sites can be seen in Figures 6-1 and 6-2, respectively. Of the cobalt sites, 400 are located within the United States, 1 is located in Guam, and 3 are located in the Commonwealth of Puerto Rico. All of the sites at which ^{60}Co has been identified are located within the United States.

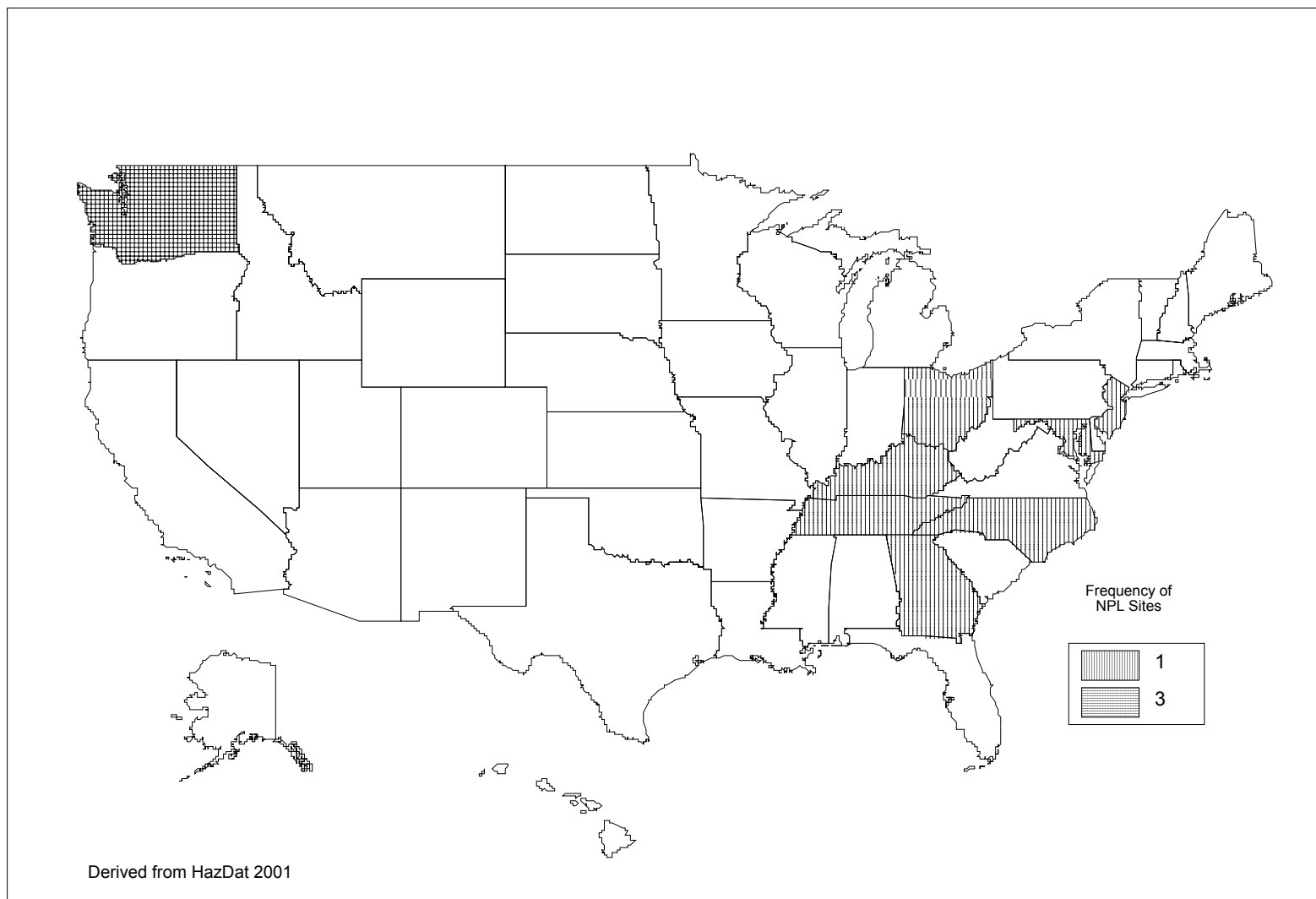
Cobalt occurs naturally in the earth's crust, and therefore, in soil. Low levels of cobalt also occur naturally in seawater and in some surface water and groundwater (Smith and Carson 1981). However, elevated levels of cobalt in soil and water may result from anthropogenic activities such as the mining and processing of cobalt-bearing ores, the application of cobalt-containing sludge or phosphate fertilizers to soil, the disposal of cobalt-containing wastes, and atmospheric deposition from activities such as the burning of fossil fuels and smelting and refining of metals (Smith and Carson 1981). Cobalt is released into the atmosphere from both anthropogenic and natural sources. However, emissions from natural sources are estimated to slightly exceed those from manufactured sources. Natural sources include windblown soil, seawater spray, volcanic eruptions, and forest fires. Primary anthropogenic sources include fossil fuel and waste combustion, vehicular and aircraft exhausts, processing of cobalt and cobalt-containing alloys, copper and nickel smelting and refining, and the manufacture and use of cobalt chemicals and fertilizers derived from phosphate rocks (Barceloux 1999; Lantzy and Mackenzie 1979; Nriagu 1989; Smith and Carson 1981). ^{60}Co and ^{58}Co may be released to the environment as a result of nuclear research and development, nuclear accidents, operation of nuclear power plants, and radioactive waste dumping in the sea or in radioactive waste landfills.

Cobalt compounds are nonvolatile and cobalt will be emitted to the atmosphere only in particulate form. Their transport in air depends on their form, particle size and density, and meteorological conditions. Cobalt so released will return to land or surface water as wet or dry deposition. Coarse particles, those with aerodynamic diameters $>2\ \mu\text{m}$ (such as those obtained during ore processing), may deposit within 10 km from the point of emission; finer particles (such as is obtained from thermal processes) may travel

Figure 6-1. Frequency of NPL Sites with Cobalt Contamination



Figure 6-2. Frequency of NPL Sites with Cobalt 60 Contamination



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longer distances. It is generally assumed that anthropogenic cobalt originating from combustion sources exists primarily as the oxide; arsenides or sulfides may be released during mining and ore processing (Schroeder et al. 1987). Sediment is the final depository for cobalt released into water. Soluble cobalt released into waterways will sorb to particles and settle into the sediment or be sorbed directly by sediment. It may precipitate out as carbonates and hydroxides or with mineral oxides. It may also sorb to or complex with humic substances in the water column. These processes are sensitive to environmental factors such as pH and the proportion of dissolved cobalt will be higher at low pH. In the case of ^{60}Co released into an experimental lake in northwestern Ontario, cobalt's half-life in the water column was 11 days; 5% of added ^{60}Co remained in the water column after 100 days (Bird et al. 1998a). Cobalt can also be transported in dissolved form or as suspended sediment by rivers to lakes and the sea or by ocean currents. The proportion of cobalt transported in each form is highly variable (Smith and Carson 1981). In deep sediment where water is anoxic and hydrogen sulfide is present, some mobilization of cobalt from sediment may occur, probably due to the formation of bisulfides and polysulfides (Bargagli 2000; Brüggmann 1988; Finney and Huh 1989; Glooschenko et al. 1981; Knauer et al. 1982; Nriagu and Coker 1980; Shine et al. 1995; Smith and Carson 1981; Szefer et al. 1996; Windom et al. 1989). Cobalt adsorbs rapidly and strongly to soil and sediment in which it is retained by metal oxides, crystalline minerals, and natural organic matter. The mobility of cobalt sediment depends on the nature of the soil or sediment; it increases with decreasing pH and redox potential (Eh) and in the presence of chelating/complexing agents (Brooks et al. 1998; Buchter et al. 1989; King 1988b; McLaren et al. 1986; Schnitzer 1969; Smith and Carson 1981; Swanson 1984; Yashuda et al. 1995).

While cobalt may be taken up from soil by plants, the translocation of cobalt from roots to above-ground parts of plants is not significant in most soils; the transfer coefficient (concentration in plant/concentration in soil) for cobalt is generally 0.01–0.3 (Mascanzoni 1989; Mermut et al. 1996, Smith and Carson 1981). However, in highly acidic soils (pH as low as 3.3) and in some higher plants, significantly higher transfer has been observed (Boikat et al. 1985; Francis et al. 1985; Jenkins 1980; Kloke et al. 1984; Mejsstrik and Svacha 1988; Palko and Yli-Hala 1988; Tolle et al. 1983; Watabe et al. 1984). The bioaccumulation factors (dry weight basis) for cobalt in marine fish and freshwater fish are ~100–4,000 and <10–1,000, respectively; accumulation is largely in the viscera and on the skin, as opposed to the edible parts of the fish. Cobalt does not biomagnify up the food chain (Barceloux 1999; Evans et al. 1988; Freitas et al. 1988; Smith and Carson 1981).

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Atmospheric cobalt is associated with particulate matter. Mean cobalt levels in air at unpolluted sites are generally $<1\text{--}2\text{ ng/m}^3$. In several open-ocean environments, geometric mean concentrations ranged from 0.0004 to 0.08 ng/m^3 (Chester et al. 1991). However in source areas, cobalt levels may exceed 10 ng/m^3 ; the highest average cobalt concentration recorded was 48 ng/m^3 at the site of a nickel refinery in Wales (Hamilton 1994; Smith and Carson 1981). By comparison, the Occupational Safety and Health Administration (OSHA) limit for airborne cobalt is $100,000\text{ ng/m}^3$. While ^{60}Co has been detected in some air samples at the Hanford site and Oak Ridge National Laboratories, levels were not reported (HazDat 2001; PNNL 1996).

The concentrations of cobalt in surface and groundwater in the United States are generally low; $<1\text{ }\mu\text{g/L}$ in pristine areas and $1\text{--}10\text{ }\mu\text{g/L}$ in populated areas (Hamilton 1994; Smith and Carson 1981). However, cobalt levels may be considerably higher in mining or agricultural areas. Cobalt levels in most drinking water is $<1\text{--}2\text{ }\mu\text{g/L}$ although levels as high as $107\text{ }\mu\text{g/L}$ have been recorded (Greathouse and Craun 1978; Meranger et al. 1981; NAS 1977; Smith and Carson 1981). Little data are available on the levels of ^{60}Co in water. In 1989, subsequent to the largest effluent discharge from the Steam Generating Heavy Water Reactor at Winfrith on the south coast of England, ^{60}Co levels in offshore seawater from 18 sites contained $0.06\text{--}2.22\text{ mBq/L}$ ($1.6\text{--}69\text{ fCi}$) of particulate ^{60}Co , $0.30\text{--}10.3\text{ mBq/L}$ ($8\text{--}280\text{ fCi}$) of soluble $^{60}\text{Co(II)}$, and $0.12\text{--}1.55\text{ mBq/L}$ ($3.2\text{--}42\text{ fCi}$) of soluble $^{60}\text{Co(III)}$ (Leonard et al. 1993a). The U.S. NRC discharge limit is $111,000\text{ mBq/L}$ (NRC 1991).

The average concentrations of cobalt in the earth's crust is $20\text{--}25\text{ mg/kg}$ (Abbasi et al. 1989; Merian 1985; Smith and Carson 1981). Most soils contain $1\text{--}40\text{ mg cobalt/kg}$; the average cobalt concentration in U.S. soils is 7.2 mg/kg (Smith and Carson 1981). Soils containing $<0.5\text{--}3\text{ mg cobalt/kg}$ are considered cobalt-deficient because plants growing on them have insufficient cobalt ($<0.08\text{--}0.1\text{ mg/kg}$) to meet the dietary requirements of cattle and sheep. Cobalt-deficient soils are found in some areas of the southeastern and northeastern United States. Soils near ore deposits, phosphate rocks, or ore smelting facilities, and soils contaminated by airport traffic, highway traffic, or other industrial pollution may contain high concentrations of cobalt; concentrations up to 800 mg/kg have been detected in such areas (Kloke et al. 1984; Smith and Carson 1981).

The level of cobalt in most foods is low. However, food is the largest source of exposure to cobalt in the general population. The estimated average daily dietary intake of cobalt in Canada was $11\text{ }\mu\text{g/day}$. Food groups contributing most heavily to this intake were bakery goods and cereals (29.8%) and vegetables

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(21.9%). No estimates of the average dietary input of cobalt in the United States was located. People living near mining and smelting facilities or metal shops where cobalt is used in grinding tools may be exposed to higher levels of cobalt in air or soil. Similarly, people living near hazardous waste sites may be exposed to higher levels of cobalt in these media. Contaminated soils pose a hazardous exposure pathway to children because of both hand-to-mouth behavior and intentional ingestion of soil (pica) that contain metals and other contaminants (Hamel et al. 1998). However, much of the cobalt in soil may not be in a form that is available for uptake by the body. People who work in the hard metal industry, metal mining, smelting, and refining or other industries that produce or use cobalt and cobalt compounds may be exposed to substantially higher levels of cobalt, mainly from dusts or aerosols in air. Workers at nuclear facilities, irradiation facilities, or nuclear waste storage sites may be exposed to radioisotopes of cobalt. Exposure would generally be to radiation produced by these isotopes (e.g., gamma radiation from ^{60}Co).

6.2 RELEASES TO THE ENVIRONMENT

Cobalt has been identified in a variety of environmental media (air, surface water, leachate, groundwater, soil, and sediment) collected at 404 of 1,585 current or former NPL hazardous waste sites (HazDat 2001). ^{60}Co has been identified in a variety of environmental media (air, surface water, leachate, groundwater, soil, and sediment) collected at 11 of 1,585 current or former NPL hazardous waste sites (HazDat 2001).

According to the Toxic Chemical Release Inventory (TRI), in 1999, total releases of cobalt and cobalt compounds to the environment (including air, water, soil, and underground injection) from 695 reporting facilities that produced, processed, or used cobalt or cobalt compounds were 15,593,293 pounds (TRI99 2001). Table 6-1 lists amounts released from these facilities grouped by state. In addition, 1,296,686 pounds of cobalt and cobalt compounds were transferred off-site by these facilities (TRI99 2001). Starting in 1998, metal mining, coal mining, electric utilities, and Resource Conservation and Recovery Act (RCRA)/solvent recovery industries are required to report to the TRI, industries with potentially large releases of cobalt and cobalt compounds. Industrial sectors producing, processing, or using cobalt that contributed the greatest environmental releases were electric utilities and RCRA/solvent recovery with 32,032 and 51,110 pounds, respectively. Industrial sectors producing, processing or using cobalt compounds that contributed the greatest environmental releases were metal mining and electrical

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Cobalt or Cobalt Compounds

State ^b	Number of facilities	Reported amounts released in pounds per year ^a						
		Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
AK	2	25	0	17,000	471,000	488,025	0	488,025
AL	23	4,510	8,792	0	361,651	374,953	25,268	400,221
AR	9	726	9	0	20,098	20,833	14,093	34,926
AZ	12	1,327	5	0	2,437,086	2,438,418	4,912	2,443,330
CA	28	472	20	0	148,671	149,163	21,603	170,766
CT	9	1,185	544	0	0	1,729	2,277	4,006
DE	2	16	101	0	100	217	10,754	10,971
FL	13	3,277	343	0	78,141	81,761	20,341	102,102
GA	21	3,387	8	0	331,435	334,830	14,962	349,792
IA	4	0	0	0	0	0	0	0
ID	2	52	5	0	47,000	47,057	0	47,057
IL	35	2,628	13,579	0	77,505	93,712	123,375	217,087
IN	33	7,730	349	0	360,677	368,756	66,125	434,881
IO	20	536	0	0	0	536	2,764	3,300
KS	5	4,806	0	0	0	4,806	6,162	10,968
KY	24	3,699	597	0	419,687	423,983	11,853	435,836
LA	14	311	8,256	8,800	42,299	59,666	42,290	101,956
MA	9	443	780	0	18	1,241	10,180	11,421
MD	5	1,007	5	0	0	1,012	1,643	2,655
ME	1	92	0	0	0	92	2,531	2,623

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Cobalt or Cobalt Compounds (continued)

State ^b	Number of facilities	Reported amounts released in pounds per year ^a						
		Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
MI	28	5,448	910	0	130,795	137,153	16,227	153,380
MN	3	20	0	0	0	20	12,859	12,879
MO	7	1,367	7	0	324,027	325,401	250	325,651
MS	11	236	467	16,000	21,945	38,648	3,995	42,643
MT	1	250	0	0	31,000	31,250	1,250	32,500
NC	28	6,999	6,504	0	211,487	224,990	15,378	240,368
ND	2	1,215	250	0	71,400	72,865	52,305	125,170
NE	1	1	28	0	0	29	4,379	4,408
NH	2	0	0	0	0	0	0	0
NJ	12	1,093	49	0	250	1,392	9,509	10,901
NM	10	591	5	0	1,852,990	1,853,586	48,052	1,901,638
NV	14	1,003	0	1	6,407,931	6,408,935	1,894	6,410,829
NY	13	1,036	59	0	4,200	5,295	14,189	19,484
OH	63	6,115	1,107	1,600	323,344	332,166	126,431	458,597
OK	10	1,537	23	0	15	1,575	53,970	55,545
OR	4	1,009	15	0	0	1,024	1,826	2,850
PA	55	13,400	1,309	0	61,176	75,885	201,959	277,844
PR	2	2	0	0	0	2	5,414	5,416
RI	1	1	1	0	0	2	26	28
SC	30	2,306	9,695	0	120,985	132,986	85,353	218,339

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Cobalt or Cobalt Compounds (*continued*)

State ^b	Number of facilities	Reported amounts released in pounds per year ^a						
		Air ^c	Water	Under-ground injection	Land	Total on-site release ^d	Total off-site release ^e	Total on and off-site release
TN	19	5,011	30,726	0	272,945	308,682	25,022	333,704
TX	51	10,102	2,930	4,021	256,594	273,647	120,010	393,657
UT	10	3,014	0	0	48,466	51,480	14,232	65,712
VA	8	1,503	1,079	0	76,000	78,582	7,041	85,623
VI	1	0	0	0	0	0	71	71
WA	2	262	98	0	44,459	44,819	5,664	50,483
WI	21	984	10	0	1,012	2,006	45,715	47,721
WV	13	1,579	709	0	259,020	261,308	42,532	303,840
WY	2	919	0	0	37,856	38,775	0	38,775
Total	695	103,232	89,374	47,422	15,353,265	15,593,293	1,296,686	16,889,979

Source: TRI99 2001

^aData in TRI are maximum amounts released by each facility.

^bPost office state abbreviations are used.

^cThe sum of fugitive and stack releases are included in releases to air by a given facility.

^dThe sum of all releases of the chemical to air, land, water, and underground injection wells.

^eTotal amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

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utilities with 11,040,532 and 3,578,014 pounds, respectively. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

6.2.1 Air

The sources of cobalt in the atmosphere are both natural and anthropogenic (Barceloux 1999). Natural sources include wind-blown continental dust, seawater spray, volcanoes, forest fires, and continental and marine biogenic emissions. The worldwide emission of cobalt from natural sources has been estimated to range from 13 to 15 million pounds/year (Lantzy and Mackenzie 1979; Nriagu 1989). The global atmospheric emission of cobalt from anthropogenic sources is an estimated 9.7 million pounds/year. Therefore, natural sources contribute slightly more to cobalt emission in the atmosphere than anthropogenic sources (Lantzy and Mackenzie 1979). The primary anthropogenic sources of cobalt in the atmosphere are the burning of fossil fuels and sewage sludge, phosphate fertilizers, mining and smelting of cobalt-containing ores, processing of cobalt-containing alloys, and industries that use or process cobalt compounds. Small amounts of cobalt are found in coal, crude oils, and oil shales. Therefore, burning of these fossil fuels for power generation will emit cobalt into the atmosphere. The cobalt contents of the fly ash and flue gases of a coal-burning power plant are approximately 25 mg/kg and 100–700 µg/L, respectively. Gasoline contains <0.1 mg cobalt/kg, but the catalytic converters may contain cobalt; therefore, emissions from vehicular exhaust are also a source of atmospheric cobalt (Abbasi et al. 1989; Holcombe et al. 1985; Ondov et al. 1982; Smith and Carson 1981). Cobalt has been detected in cigarette tobacco and therefore, smoking is a potential source of cobalt emissions that could impact on indoor air quality (Munita and Mazzilli 1986).

Cobalt has been identified in air samples collected at 5 of the 404 current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2001). ⁶⁰Co has been identified in air samples collected at 2 of the 11 current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2001).

Air sampling data were used to estimate ⁶⁰Co release from the Savannah River Site (SR) from the plant's start up in 1954 to 1989 (DOE 1991). From this monitoring, it was estimated that 0.092 Ci of ⁶⁰Co was released to the atmosphere between 1968 and 1986. SR was a major production facility to the U.S. defense program and included five nuclear reactors, a fuel and target fabrication plant, a naval fuel materials facility, two chemical separation plants, a heavy water production plant, and a laboratory. ⁶⁰Co

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has also been detected in air samples at the Hanford site and Oak Ridge National Laboratories (HazDat 2001; PNNL 1996).

According to the TRI, in 1999, releases of 103,232 pounds of cobalt and cobalt compounds to air from 695 reporting facilities accounted for 0.7% of the total on-site environmental releases of these substances (TRI99 2001). The industrial sectors contributing the largest release of cobalt and cobalt compounds to air were electrical utilities, primary metals and chemicals. Table 6-1 lists the amounts of cobalt and cobalt compounds released to air from these facilities grouped by state. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

6.2.2 Water

Compounds of cobalt occur naturally in seawater and in some surface, spring, and groundwater (Smith and Carson 1981). Cobalt is also released into water from anthropogenic sources. While there has been no mine production of cobalt in the United States in recent years, cobalt is a byproduct or coproduct of the refining of other mined metals such as copper and nickel. Waste water from the recovery of cobalt from imported matte or scrap metal, refining of copper and nickel, or during the manufacture of cobalt chemicals are sources of cobalt in water (Smith and Carson 1981). Process water and effluent from coal gasification and residue from solvent-refined coal contain cobalt. The accidental discharge of activated sludge and sewage may be an important sources of cobalamins in waterways, together with bioconcentration by benthic organisms (Smith and Carson 1981). The discharge of waste water by user industries, such as paint and pigment manufacture, also contribute to the release of cobalt into water. In one case, manufacturers of nickel-cadmium batteries operating between 1953 and 1979 discharged cobalt from a battery factory to the Hudson River in Foundry Cove, New York, of which 1.2 MT are estimated to be present in the eastern cove (Knutson et al. 1987). Atmospheric deposition is an additional source of cobalt in water. Lake Huron receives an estimated 76% of its cobalt input from natural sources and 24% from anthropogenic sources. The corresponding estimated values for Lake Superior are 85.4 and 14.6% (Smith and Carson 1981). In these Great Lakes, it therefore appears that natural inputs of cobalt far exceeds anthropogenic ones.

Cobalt has been identified in groundwater and surface water at 242 and 98 sites, respectively, of the 404 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2001). ⁶⁰Co

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has been identified in groundwater and surface water at 3 and 2 sites, respectively, of the 11 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2001).

According to the TRI, in 1999, the reported releases of 89,374 pounds of cobalt and cobalt compounds to water from 695 reporting facilities accounted for 0.6% of the total on-site environmental releases of these substances (TRI99 2001). Table 6-1 lists the amounts of cobalt and cobalt compounds released to water from these facilities grouped by state. As of 1998, TRI no longer separately collects data on substances released indirectly to Publicly-Owned Treatment Works (POTWs), part of which may ultimately be released to surface waters. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

^{60}Co is present in the low-level aqueous radioactive waste discharges from many nuclear power plants. Cobalt-containing alloys used in piping of nuclear reactors corrode and may be activated, producing ^{60}Co which accumulates in the reactor and must be periodically decontaminated. A common decontaminating agent includes a reducing metal ion (e.g., vanadium(II)) and a chelating agent (e.g., picolinate) resulting in low-level discharges of uncomplexed $^{60}\text{Co(II)}$ and complexed $^{60}\text{Co(III)}$. While soluble ionic and particulate forms predominate, at some sites stable, nonionic trivalent complexes of cobalt are present (Leonard et al. 1993b). For example, in 1987–1989 samples of treated effluent from the Steam Generating Heavy Water Reactor at Winfrith on the south coast of England, the percent of ^{60}Co as Co(III) picolinate ranged from 6.2 to 75.4%. Between 1978 and 1988, 12 TBq (320 Ci) of ^{60}Co was released into the Irish Sea by the British Nuclear Fuels reprocessing plant at Sellafield, United Kingdom (McCartney et al. 1994). These discharges are believed to be Co(II) (Leonard et al. 1993a). Both ^{58}Co and ^{60}Co are discharged into the Rhone River by the nuclear power plant at Bugey, France. This facility, which consists of a natural Uranium-Graphite-Gas unit and four pressurized water reactor (PWR) units, two of which are cooled by Rhone River water, discharged about 406 and 280 GBq (11.0 and 7.56 Ci) of ^{58}Co and ^{60}Co , respectively, in liquid waste during 1986–1990 (Beaugelin-Seiler et al. 1994).

Water sampling data were used to estimate effluent release from the SR Site from the plant's start up in 1954 to 1989 (DOE 1991). From this monitoring, it was estimated that 17.8 Ci (659 GBq) of ^{60}Co were released into seepage basins and 66.4 Ci (2,460 GBq) were released into streams between 1955 and 1988. In addition, 2.7 Ci (100 GBq) of ^{58}Co were released into seepage basins between 1971 and 1988; no ^{58}Co was released into streams. ^{60}Co has also been reported in surface water and groundwater at the Hanford site and Oak Ridge National Laboratories (HazDat 2001; PNNL 1996). The Columbia River receives

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discharges from the unconfined aquifer underlying the Hanford Site via subsurface and surface (riverbank springs) discharges. This aquifer is contaminated by leachate from past waste-disposal practices at the site.

6.2.3 Soil

Cobalt occurs naturally in the earth's crust, and therefore, in soil. However, elevated levels of cobalt in soil may result from anthropogenic activities such as the mining and processing of cobalt-bearing ores, the application of cobalt-containing sludge or phosphate fertilizers to soil, the disposal of cobalt-containing wastes, and atmospheric deposition from activities such as the burning of fossil fuels, smelting, and metal refining (Smith and Carson 1981).

Cobalt has been identified in soil at 203 sites and sediment at 134 sites collected from 404 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2001). ⁶⁰Co has been identified in soil at 6 sites and sediment at 2 sites collected from 11 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2001).

According to the TRI, in 1999, reported releases of 15,353,265 pounds of cobalt and cobalt compounds to land from 695 reporting facilities accounted for 98.5% of the total on-site environmental releases of these substances (TRI99 2001). An additional 47,422 pounds, accounting for 0.2% of the total on-site environmental releases were injected underground (TRI99 2001). Industrial sectors contributing the largest releases of cobalt and cobalt compounds to land were metal mining and electrical utilities with 11,022,063 and 3,541,815 pounds, respectively. Table 6-1 lists the amounts of cobalt and cobalt compounds released on land from these facilities grouped by state. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

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6.3 ENVIRONMENTAL FATE**6.3.1 Transport and Partitioning**

Cobalt compounds are nonvolatile, and thus cobalt is emitted to the atmosphere in particulate form. The transport of cobalt in air depends on its form, particle size and density, and meteorological conditions; it returns to land or surface water as wet or dry deposition. In nonarid areas, wet deposition may exceed dry deposition (Arimoto et al. 1985; Erlandsson et al. 1983). Coarse particles, with aerodynamic diameters $>2\ \mu\text{m}$ (such as those obtained during ore processing), may deposit within 10 km from the point of emission; finer particles may travel longer distances. It is the larger particles that may be responsible for elevated local concentrations around emission sources. The mass median diameter for cobalt particles emitted from a power generator with a stack emission controlled by an electrostatic precipitator or scrubber ranged from <2 to $12\ \mu\text{m}$. The mass median diameter of cobalt in the ambient atmosphere is about $2.6\ \mu\text{m}$ (Milford and Davidson 1985). Golomb et al. (1997) report average total (wet + dry) deposition rates of cobalt to Massachusetts Bay during the period September 15, 1992 to September 16, 1993. The total deposition rate was $58\ \mu\text{g}/\text{m}^2\text{-year}$ of which $47\ \mu\text{g}/\text{m}^2\text{-year}$ was dry deposition and $12\ \mu\text{g}/\text{m}^2\text{-year}$ was wet deposition. Total cobalt deposition flux at a site in the Rhone delta in southern France in 1988–1989 was $0.42\pm0.23\ \text{kg}/\text{km}^2\text{-year}$ with $0.15\ \text{kg}/\text{km}^2\text{-year}$ in the form of wet deposition (Guieu et al. 1991).

As with most metals, sediment and soil are the final repository for cobalt released into the environment. Cobalt released into waterways will sorb to particles and settle into the sediment or be sorbed directly into the sediment. It can also be transported in dissolved form or as suspended sediment by rivers to lakes and the sea or by ocean currents. Sediment in areas of active sedimentation would receive a large portion of the suspended sediment. In the case of the Peach Bottom Atomic Power Plant where ^{60}Co is released into the Conowingo Reservoir, an impoundment of the lower Susquehanna River, $<20\%$ of the radionuclide is trapped in the reservoir sediment, the rest being transported downstream and into the Chesapeake Bay (McLean and Summers 1990). It is often assumed that the primary mode of transport of heavy metals in aquatic systems is as suspended solids (Beijer and Jernelov 1986). However, in the case of cobalt, the percent that is transported in suspended solids is highly variable. Examples of the percentage of cobalt transported in suspended solids include (water body, percent): Main River (Germany), 33.4–42.2%; Susquehanna River (near its source in New York), 9%; New Hope River (North Carolina), 92%; Yukon River, $>98\%$; Danube River (1961–1970), 27.4–85.9%; Columbia River (^{60}Co , downstream of the Hanford

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site), 95–98%; Strait of Juan de Fuca (Puget Sound, Washington), 11–15%; North Sea, 34%; and Lake Washington (Washington), 0% (Smith and Carson 1981).

In the oxic zones of many surface waters, dissolved cobalt levels decrease with increasing depth. This may be due to cobalt's continuous input into surface water from discharges or to increased adsorption and precipitation of the soluble forms with increasing depth. The fact that cobalt concentration profiles in deep water follow manganese and aluminum profiles strongly suggests that dissolved cobalt is precipitated in the adsorbed state with oxides of iron and manganese and with crystalline sediments such as aluminosilicate and goethite. A part of the cobalt may also precipitates out as carbonate and hydroxide in water. In large unpolluted rivers, cobalt was found in the following forms: dissolved, 1.6–1.7%; adsorbed, 4.7–8.0%; precipitated and coprecipitated with mineral oxides such as iron and manganese, 27.3–29.2%; precipitates such as carbonate and hydroxides, 12.9–19.3%; and in crystalline sediment minerals such as aluminosilicate and goethite, 43.9–51.4%. The corresponding fractions in a contaminated river were 12.2, 27.4, 19.2, 14.6, and 26.5%. The higher concentration of organic pollutants in polluted water probably results in the formation of higher concentrations of soluble organic complexes. In a deep sediment where the water was anoxic and contained hydrogen sulfide, some mobilization of cobalt was observed, probably due to the formation of bisulfide and polysulfide complexes (Bargagli 2000; Brüggmann 1988; Finney and Huh 1989; Glooschenko et al. 1981; Knauer et al. 1982; Nriagu and Coker 1980; Shine et al. 1995; Smith and Carson 1981; Szefer et al. 1996; Windom et al. 1989).

Cobalt strongly binds to humic substances naturally present in aquatic environments. The lability of the complexes is strongly influenced by pH, the nature of the humic material, and the metal-to-humic substance ratio. The lability of cobalt-humate complexes decreases in time (“aging effect”) (Burba et al. 1994). The “aging effect” indicates that after a period of time (~12 hours) complexes that were initially formed are transformed into stronger ones from which the metal ion is less readily dislodged. In the Scheldt Estuary and the Irish Sea, between 45 and 100% of dissolved cobalt was found to occur in these very strong complexes (Zhang et al. 1990). Aquifer material from the contaminated aquifer at a low-level infiltration pit at the Chalk River Nuclear Laboratories in Canada was analyzed to assess the nature of the adsorbed ^{60}Co using sequential leaching techniques (Killey et al. 1984). Of the sediment-bound ^{60}Co , <10% was exchangeable, 5–35% was retained by iron oxide, and 55–>90% was fixed. Over 80% of the dissolved ^{60}Co was present as weakly anionic hydrophilic organic complexes. The average K_d for ^{60}Co between particulate matter and Po River (Italy) water was 451 m^3/kg over a 2-year monitoring period

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(Pettine et al. (1994). The mean K_d for ^{60}Co in Arctic surface sediment (Kara Sea) where large quantities of radioactive waste by the former Soviet Union was disposed was 1×10^5 L/kg (range 1×10^3 – 7×10^5), which is comparable to that in temperate coastal regions, 2×10^5 L/kg (range, 2×10^4 – 1×10^6) (Fisher et al. 1999).

The distribution coefficient of cobalt may vary considerably in the same sediment in response to conditions affecting the pH, redox conditions, ionic strength, and amount of dissolved organic matter (Mahara and Kudo 1981). Uptake of ^{60}Co from the water column by sediment increased rapidly as the pH was increased from 5 to pH 7–7.5 and then slightly decreases (Benes et al. 1989a, 1989b). Therefore, pH would be an important factor affecting the migration of cobalt in surface water. Uptake was little affected by changes in liquid-to-solids ratio and ionic strength. ^{60}Co is more mobile in anaerobic marine aquatic environments than in freshwater aerobic ones (Mahara and Kudo 1981). Therefore, ^{60}Co waste is most suitably stored underground in aerated zones away from possible seawater intrusions. In seawater-sediment systems under anaerobic conditions ^{60}Co was 250 times more mobile than ^{60}Co in freshwater-sediment systems under aerobic conditions. Under anaerobic conditions, 30% of the ^{60}Co added to a sediment-freshwater system was ‘exchangeable’ and therefore potentially mobile, while under aerobic conditions, 98% of the ^{60}Co was permanently fixed. Most of the mobile ^{60}Co produced under anaerobic conditions in seawater consisted of nonionic cobalt associated with low molecular weight organic substances that were stable to changes in pH; the exchangeable ^{60}Co appeared to be mostly ionic.

Bird et al. (1998b) added ^{60}Co to the anoxic hypolimnion of a Canadian Shield lake to simulate a nuclear waste scenario where radionuclides entered the bottom waters of a lake, and evaluated its behavior over 5 years. This situation was considered to be a likely pathway by which nuclear fuel waste stored deep underground in the plutonic rock of this region would reach the surface environment via deep groundwater flow into the bottom waters of a lake. It was felt that adding a redox sensitive element such as cobalt to the anoxic hypolimnion might be different from adding it to the epilimnion. Monitoring vertical profiles in the lake established that the cobalt remained confined to the anoxic hypolimnion prior to the fall turnover (first 72 days) when mixing occurred throughout the water column. By day 358, only about 4% of the ^{60}Co remained in the water column. After the second year, approximately 2% of the ^{60}Co remained and after 5 years, only 0.4%. These results mirror previous experiments in which the ^{60}Co was added to the epilimnion, therefore establishing that there is little difference in the overall behavior of cobalt when added to the epilimnion or hypolimnion. The loss rate coefficient of ^{60}Co was 0.036/day ($t_{1/2}=19$ days) between days 90 and 131 (lake mixing) during which time, the cobalt sorbed to the

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suspended sediment and bottom sediment under anoxic conditions. Loss was to the sediment as there was no hydrological loss from the lake. In the previous experiment in which ^{60}Co was added to the epilimnion, the initial loss rate coefficient was somewhat higher, 0.056/day ($t_{1/2}=12$ days). Following the initial loss, ^{60}Co continued to be slowly removed from the water column (loss rate coefficient 0.002/day; $t_{1/2}=347$ days); after 328 days, ^{60}Co was no longer detectable in the epilimnion. The half life of ^{60}Co in the water column of an experimental lake in northwestern Ontario was 11 days; 5% of added ^{60}Co remained in the water column after 100 days (Bird et al. 1998b). The redox potential also affects the behavior of cobalt in sediment. Under moderately reducing conditions, cobalt is released from sediment as Co^{2+} and forms CoS in the presence of sulfide. The concentration of cobalt in the bottom water increases as the water becomes more anoxic (Brügmann 1988; Smith and Carson 1981).

The mobility of cobalt in soil is inversely related to how strongly it is adsorbed by soil constituents. Cobalt may be retained by mineral oxides such as iron and manganese oxide, crystalline materials such as aluminosilicate and goethite, and natural organic substances in soil. Sorption of cobalt to soil occurs rapidly (within 1–2 hours). Soil-derived oxide materials adsorb were found to adsorb greater amounts of cobalt than other materials examined, although substantial amounts were also adsorbed by organic materials. Clay minerals sorbed relatively smaller amounts of cobalt (McLaren et al. 1986). In addition, little cobalt was desorbed from soil oxides while substantial amounts desorbed from humic acids and montmorillonite. In clay soil, adsorption may be due to ion exchange at the cationic sites on clay with either simple ionic cobalt or hydrolyzed ionic species such as CoOH^+ . Adsorption of cobalt onto iron and manganese increases with pH (Brooks et al. 1998). In addition, as pH increases, insoluble hydroxides or carbonates may form, which would also reduce cobalt mobility. Conversely, sorption onto mobile colloids would enhance its mobility. In most soils, cobalt is more mobile than lead, chromium (II), zinc, and nickel, but less mobile than cadmium (Baes and Sharp 1983; King 1988b; Mahara and Kudo 1981; Smith and Carson 1981). In several studies, the K_d of cobalt in a variety of soils ranges from 0.2 to 3,800. The geometric mean, minimum, median, and maximum K_d s of ^{60}Co in 36 Japanese agricultural soils were 1,840, 130, 1,735, and 104,000 L/kg, respectively (Yasuda et al. 1995). The soil properties showing the highest correlation with K_d were exchangeable calcium, pH, water content, and cation exchange capacity (CEC). In 11 U.S. soils, the mean Freundlich K_F and n values were 37 L/kg and 0.754, respectively; K_F values ranged from 2.6 to 363 L/kg and correlated with soil pH and CEC (Buchter et al. 1989). In 13 soils from the southeastern United States whose soil pH ranged from 3.9 to 6.5, cobalt sorption ranged from 15 to 93%; soil pH accounted for 84–95% of the variation in sorption (King 1988b).

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Organic complexing agents such as ethylenediaminetetraacetic acid (EDTA), which are used for decontamination operations at nuclear facilities, greatly enhance the mobility of cobalt in soil. Other organic complexing agents, such as those obtained from plant decay, may also increase cobalt mobility in soil. However, both types of complexes decrease cobalt uptake by plants (Killey et al. 1984; McLaren et al. 1986; Toste et al. 1984). Addition of sewage sludge to soil also increases the mobility of cobalt, perhaps due to organic complexation of cobalt (Gerritse et al. 1982; Williams et al. 1985).

Leaching of cobalt has been observed from municipal and low-level radioactive waste sites (Cyr et al. 1987; Czyscinski et al. 1982; Friedman and Kelmers 1988). The mobility of cobalt was assessed in two soils from the Cabriole and Little Feller event sites at the Nevada Test site as a function of various parameters such as pH, ionic strength, cobalt concentrations, soil solids concentrations, and particle size distribution (DOE 1996). Cobalt was quantitatively sorbed on these soils (at least 90% sorbed) when the pH was above 7 and the solid concentration was at least 20 g/L. The experiments suggest that binding is principally on amphoteric surface-hydroxyl surfaces. Since the pH of these soils is around 8, cobalt would bind strongly under normal environmental conditions. Migration would be severely retarded under all but the most extreme conditions, e.g., pH of 4 or below and high ionic strength soil solutions (approximately 0.1 M). In addition, unrealistically large quantities of water would be needed to displace cobalt from the upper layers of the soil profile.

Cobalt may be taken up from soil by plants. Surface deposition of cobalt on leaves of plants from airborne particles may also occur. Elevated levels of cobalt have been found in the roots of sugar beets and potato tubers in soils with high cobalt concentrations (e.g., fly ash-amended soil) due to absorption of cobalt from soil. However, the translocation of cobalt from roots to above-ground parts of plants is not significant in most soils, as indicated by the lack of cobalt in seeds of barley, oats, and wheat grown in high-cobalt soil (Mermut et al. 1996; Smith and Carson 1981). Mermut et al. (1996) found 0.01–0.02 mg/kg in 10 samples of durum wheat grain from different areas of Saskatchewan where surface soil cobalt levels ranged from 3.7 to 16.4 mg/kg. The enrichment ratio, defined as the concentration in a plant grown in amended soil (fly ash) over the concentration in unamended soil, was about 1. Other authors have determined the transfer coefficient (concentration in plant/concentration in soil) for cobalt to be 0.01–0.3. The mean ^{57}Co soil-plant transfer factors obtained for clover from eight soils over a 4-year period ranged from 0.02 to 0.35, in good agreement with results of other investigators (Mascanzoni 1989). However, in highly acidic soil (pH as low as 3.3), significantly higher than normal concentrations of cobalt were found in rye grass foliage, oats, and barley. For example, cobalt concentrations in rye

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grass grown in unlimed soil (pH <5.0) was 19.7 mg/kg compared with 1.1 mg/kg in rye grass grown in limed soil (pH >5.0) (Boikat et al. 1985; Francis et al. 1985; Kloke et al. 1984; Mejstrik and Svacha 1988; Palko and Yli-Hala 1988; Tolle et al. 1983; Watabe et al. 1984). Soil and plant samples taken in the 30-km zone around Chernobyl indicated that ^{60}Co was not accumulated by plants and mushrooms (Lux et al. 1995). Transfer factors obtained in 1992 ranged from 0.005 to 0.16 and those obtained in 1993 ranged from <0.001 to 0.008.

^{60}Co is taken up by phytoplankton and unicellular algae (*Senenastrium capricornutum*) with concentration factors (dry weight) ranging from 15,000 to 40,000 and 2,300 to 18,000, respectively (Corisco and Carreiro 1999). Elimination experiments with the algae indicate a two component biological half-life, 1 hour and 11 days, respectively, and suggests that the cobalt might be absorbed not only on the surface, but also intracellularly. Since these organisms are at the bottom of the food chain, they could play an important role in the trophic transfer of ^{60}Co released into waterways by nuclear facilities. However, cobalt levels generally diminish with increasing trophic levels in a food chain (Smith and Carson 1981). The low levels of cobalt in fish may also reflect cobalt's strong binding to particles and sediment. The bioaccumulation factors (dry weight basis) for cobalt in marine and freshwater fish are ~100–4,000 and <10–1,000, respectively; accumulation in the muscle of marine fish is 5–500 (Smith and Carson 1981). Cobalt largely accumulates in the viscera and on the skin, as opposed to the edible parts of the fish. In carp, accumulation from water accounted for 75% of ^{60}Co accumulated from both water and food; accumulation from water and food was additive (Baudin and Fritsch 1989). Depuration half-lives were 53 and 87 days for fish contaminated from food and water, respectively. In the case of an accidental release of ^{60}Co into waterways, the implication is that effects would manifest themselves rapidly since the primary route of exposure is from water rather than food. Uptake of ^{60}Co by biota in lakes in northwestern Ontario was not affected by the trophic status of the lakes (Bird et al. 1998a). Uptake of ^{60}Co was very low in whitefish, with concentrations being highest in kidney and undetectable in muscle. Similarly, while accumulation of ^{60}Co by carp from food was dependent on food type, the transfer factor was very low, approximately 0.01, and no long term bioaccumulation of the radionuclide occurred (Baudin and Fritsch 1987; Baudin et al. 1990). In the experiment described above in which Bird et al. (1998a) added ^{60}Co to the anoxic hypolimnion of a Canadian Shield lake to simulate a nuclear waste scenario where radionuclides entered the bottom waters of a lake, ^{60}Co levels in biota were low because of the rapid loss of cobalt to the sediment. Levels in forage fish, minnows, and sculpins were low, <0.3 Bq/g (8 pCi/g) dry weight; an occasional high level, ~4 Bq/g (110 pCi/g) dry weight, in slimy sculpin was thought to reflect the presence of detritus in the gut of the fish. Epilimnion additions of ^{60}Co

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in an earlier study resulted in lower maximum concentrations in fish, 0.07, 0.11, and 0.01 Bq/g (2, 3.0, and 0.3 pCi/g) dry weight in pearl dace, fathead minnows, and slimy sculpins, respectively, when similar quantities of radiocobalt were added to the lake.

Freshwater mollusks have concentration factors of 100–14,000 (~1–300 in soft tissue). Much of the cobalt taken up by mollusks and crustaceae from water or sediment is adsorbed to the shell or exoskeleton; very little cobalt is generally accumulated in the edible parts (Amiard and Amiard-Triquet 1979; Smith and Carson 1981). However, the digestive glands of crustaceans, which are sometimes eaten by man, may accumulate high levels of ^{60}Co . Five different species of marine mollusks had whole-body ^{60}Co concentration factors between 6.3 and 84 after 1 month exposure to ^{60}Co in seawater (Carvalho 1987). The shell accounted for more than half of the body-burden. Among the soft tissue, the gills and viscera had the highest concentrations factors and the muscle had the lowest. Fisher et al. (1996) studied the release of ^{60}Co accumulated in mussels from water and ingested phytoplankton. In both cases, there was a slow and fast component to the release; the rapid release was in the form of fecal pellets if uptake was from food and from desorption from the shell if uptake was from the dissolved phase. Biological half-lives obtained in laboratory studies were about 12–21 days from both the shell and soft parts. Higher absorption efficiencies and lower efflux rates were obtained for cobalamine than for inorganic cobalt suggesting that it is a more bioavailable form of cobalt for mussels. Cobalt from fecal pellets is rapidly released into the overlying water and may play a role in its geochemical cycling (Fisher et al. 1996). The concentration of cobalt in clams in the Indian River Lagoon, Florida did not correlate with levels found in either water or sediment (Trocine and Trefry 1996).

6.3.2 Transformation and Degradation

6.3.2.1 Air

There is a paucity of data in the literature regarding the chemical forms of cobalt in air and their transformations in the atmosphere. It is generally assumed that anthropogenic cobalt originating from combustion sources exists primarily as the oxide (Schroeder et al. 1987). In addition, cobalt may be released into the atmosphere as its arsenide or sulfide during ore extraction processes. It is not clear if these species are transformed in the atmosphere. Should a relatively insoluble species such as the oxide be transformed into a more soluble form such as the sulfate, one would expect greater quantities to be washed out of the atmosphere in rain.

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6.3.2.2 Water

Many factors control the speciation and fate of cobalt in natural waters and sediments. These include the presence of organic ligands (e.g., humic acids, EDTA), the presence and concentration of anions (Cl^- , OH^- , CO_3^{2-} , HCO_3^- , SO_4^{2-}), pH, and redox potential (Eh). Modeling the chemical speciation of a metal in water depends upon the environmental factors assumed and the stability constants of the various complexes. Mantoura et al. (1978) predicted the equilibrium levels of Co^{2+} species in fresh water to follow the order: free Co^{2+} \approx CoCO_3 $>$ CoHCO_3^+ \gg CoSO_4 \approx $\text{Co}\cdot\text{humic acid}$. However, the mole percent of various cobalt species in a Welsh lake was found to be: free Co^{2+} , 76%; CoCO_3 , 9.8%; CoHCO_3^+ , 9.6%; humate complexes, 4.0%; and CoSO_4 , 0.4%. The rank order of species concentration in seawater was estimated to be: $\text{CoCO}_3 >$ free $\text{Co}^{2+} >$ $\text{CoSO}_4 \approx \text{CoHCO}_3^+$. In another model, the speciation of cobalt was completely different with $\text{CoCl}^+ >$ free $\text{Co}^{2+} >$ $\text{CoCO}_3 >$ CoSO_4 (Smith and Carson 1981). More recently, Tipping et al. (1998) estimated the equilibrium speciation of cobalt in riverine, estuarine, and marine surface water of the Humber system (England). In all but seawater, cobalt complexes with carbonate (HCO_3^- and CO_3^{2-}) constituted about 70% of dissolved cobalt while the free Co^{2+} ion, was a major species, ~25%, which is much lower than the 61% predicted by Mantoura et al. (1978). As the alkalinity of the water increases, the proportion of cobalt complexed with carbonate increases at the expense of free Co^{2+} . The proportion of cobalt that exists as the free ion and the carbonate complexes in river water is independent of the level of fulvic acid in the water. In seawater, the carbonate species and the free aquo species assume roughly equal importance. The proportion of dissolved cobalt complexed with fulvic acid decreased with increasing salinity. About 20% of cobalt in seawater was estimated to be present as complexes with sulfate. In a bioconcentration study in which CoCl_2 was initially added to the seawater, at month's end, the cationic form of cobalt was progressively converted into anionic and neutral forms possibly as a result of complexation with organic ligands (Carvalho 1987). Addition of humic acid to natural waters may merely increase the concentration of colloidal dispersed metal rather than form truly soluble humic complexes. In water that contains high organic wastes such as was the case in the Rhone River in France, cobalt was almost completely complexed. Cobalt forms complexes with EDTA that are very stable environmentally. EDTA is often used in agriculture, food and drug processing, photography, and textile and paper manufacturing and therefore, it is a likely constituent of industrial discharges.

The adsorption of cobalt by particulate matter decreases with decreasing pH. This may lead to increased concentrations of dissolved cobalt at low pH. The effect of Eh on the speciation of cobalt has been shown

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by the increase in the concentration of dissolved cobalt by orders of magnitude with increasing depth in certain parts of Baltic waters. The increase in the concentration of dissolved cobalt may be due to the formation of soluble bisulfide and polysulfide complexes in the anoxic zones. The residence time of soluble cobalt in seawater has been estimated to range from <1 to 52 years (Brugmann 1988; Knauer et al. 1982; Smith and Carson 1981).

Vitamin B₁₂ is synthesized by 58 species of seven genera of bacteria as well as blue-green algae and actinomycetes. Consequently, vitamin B₁₂ levels in marine water range from very low levels in some open ocean water to much higher levels in some coastal waters. Freshwater environments have comparable levels of vitamin B₁₂. The high level of cobalamins in coastal water appears to be related to the occurrence of macrophytes in these areas with their high concentrations of vitamin B₁₂. Cobalamins are released into the water when the organisms die (Smith and Carson 1981).

Alkaline thermal groundwater in granitic areas that have been studied as possible waste disposal sites for radioactive waste (Alaux-Negrel et al. 1993). Water in these areas is characterized by high pH, low CO₂ partial pressure, and generally low redox potential; sulfide concentrations are around a few 10⁻⁴ to 10⁻³ mol/L. The solubility of cobalt is controlled by the solubility of CoS (log K₁ and log K₂ being 5.7 and 8.7 at 25 EC) and therefore, levels of cobalt are very low, 10⁻⁸–10⁻¹⁰ mol/L.

The ⁶⁰Co (III) picolinate complex that is released into water by some nuclear reactors does not break down immediately on release into seawater, but rather can coexist with the ⁶⁰Co (II) forms for lengthy periods in the environment (Leonard et al. 1993a, 1993b). Studies indicate that several processes occur to the Co(III) organic complexes, including reduction to the inorganic form, sorption of both species to particulate matter, and transformations of the uncomplexed species. It is possible that this more soluble and uncharged form of radiocobalt will increase the dispersion of ⁶⁰Co from its point of discharge.

6.3.2.3 Sediment and Soil

The speciation of cobalt in soil or sediment depends on the nature of the soil or sediment, concentration of chelating/complexing agents, pH, and redox potential (Eh) of the soil. Dissolved cobalt may be absorbed by ion exchange and other mechanisms, or form complexes with fulvic acids, humic acid, or other organic ligands in soil. The humic and fulvic complexes of cobalt are not very stable compared with those of copper, lead, iron, and nickel. The speciation of cobalt in sediment from nine sites in the Red Sea, a sea

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which is unique in that it has no permanent streams flowing into it, was assessed using a sequential extraction technique (Hanna 1992). The mean percentages contained in the various fractions were: exchangeable, 5.5%; carbonate, 5%; Fe/Mn oxides, 24%; organic, 30.4%; sulfides, 13%; and lithogenous, 22%. While the mean concentration of cobalt in the sediment increased from 0.003 to 0.006 ppb between 1934 and 1984, its distribution among the different phases did not change appreciably.

The reduction of soil Eh, which may occur when soil is flooded or in deeper layers of soil that are oxygen-depleted, may change the speciation of cobalt. This may result in the reduction of soil iron and manganese and the subsequent release of adsorbed cobalt from the mineral oxides. Similarly, a decrease in soil pH may result in the solubilization of precipitated cobalt and the desorption of sorbed cobalt resulting in increased cobalt mobility (Smith and Carson 1981). Co^{2+} may also be oxidized to Co^{3+} by manganese oxides, a common component of soils and aquifer material, with subsequent surface precipitation (Brusseau and Zachara 1993). This process may affect transport of cobalt in the subsurface environment.

EDTA complexes of cobalt are very stable and are likely to form in soils containing EDTA. EDTA is widely used as a decontaminating agent at nuclear facilities. Although cobalt-EDTA complexes are adsorbed by some soils, the mobility of cobalt in soil may increase as a result of complex formation (Schnitzer 1969; Smith and Carson 1981; Swanson 1984). ^{60}Co that is disposed of in shallow land trenches have sometimes been found to migrate more rapidly than expected from the disposal sites. Organic chelating agents are frequently present at these sites and would possibly increase the solubility and transport of the radionuclide.

Bacterial action can affect the mobility of a substance by mediating reactions or by participating in reactions that lower the pH. Another way of influencing radionuclide mobility is by degrading complexing agents used in cleaning reactors (e.g., citric acid), thereby releasing the radionuclide. However, experiments on the fate and transport of cobalt released upon the biodegradation of the complexing ligand indicate that results are not always predictable; the means of ligand removal and the geochemical environment are important factors that must be considered (Brooks et al. 1998).

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6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Cobalt concentrations in environmental media, including food and human tissue, have been exhaustively tabulated by Smith and Carson (1981) and Young (1979). The International Agency for Research on Cancer (IARC 1991) contains reviews of more recent studies, but is primarily focused on occupational exposures and body burdens of cobalt.

6.4.1 Air

Atmospheric cobalt is associated with particulate matter. Mean cobalt levels in air at unpolluted sites are generally <1 to 2 ng/m^3 (Hamilton 1994, Smith and Carson 1981). At the South Pole, cobalt levels of $0.00049 \pm 0.00015 \text{ ng/m}^3$ were recorded in 1974–1975 (Maenhaut et al. 1979). Geometric mean cobalt levels in several open-ocean environments ranged from 0.0004 to 0.08 ng/m^3 (Chester et al. 1991). The average annual PM-10 (particles with diameters $<10 \text{ }\mu\text{m}$) cobalt concentration at Nahant, Massachusetts (near Boston) in 1992–1993 was 1.7 ng/m^3 (Golomb et al. 1997). Half of the cobalt was contained in fine particles ($<2.5 \text{ }\mu\text{m}$) and half in coarse particles ($2.5\text{--}10 \text{ }\mu\text{m}$). The mean cobalt level in southern Norway in 1985–1986 ($n=346$) was 0.10 ng/m^3 with 35% of the samples falling below the detection limit of 0.04 ng/m^3 (Amundsen et al. 1992). Atmospheric cobalt levels in industrial settings may exceed 10 ng/m^3 . The highest recorded average cobalt concentration in air was 48 ng/m^3 at the site of a nickel refinery in Clydach, Wales (Smith and Carson 1981). Some ambient atmospheric levels of cobalt are given in Table 6-2. These data show the contribution of anthropogenic sources in increasing the level of cobalt in the ambient air. Typical occupational cobalt levels are $0.01\text{--}1.7 \text{ mg/m}^3$ (Barceloux 1999; IARC 1991). While ^{60}Co has been detected in air samples at the Hanford site and Oak Ridge National Laboratories, levels were not reported (HazDat 2001; PNNL 1996). In 1995, the concentration of ^{60}Co in air at the Hanford site was below the detection limit in over 88% of the air samples.

6.4.2 Water

The concentrations of cobalt in surface water and groundwater in the United States are generally low, $<1 \text{ }\mu\text{g/L}$ in pristine areas and $1\text{--}10 \text{ }\mu\text{g/L}$ in populated areas (Hamilton 1994; Smith and Carson 1981). However, cobalt levels may be considerably higher in mining or agricultural areas. Levels as high as $4,500 \text{ }\mu\text{g/L}$ were reported in Mineral Creek, Arizona, near a copper mine and smelter; levels of $6,500 \text{ }\mu\text{g/L}$ were reported in the Little St. Francis River, which receives effluent from cobalt mining and

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Table 6-2. Concentration of Cobalt in the Atmosphere

Location	Possible source/activity	Concentration ^a	Units	Type	Reference	
<i>Ambient levels - remote</i>						
South Pole, 1974–1975	Crustal material	0.00049±0.00015	ng/m ³	Mean±SD	Maenhaut et al. 1979	
Open-ocean		0.0004–0.08	ng/m ³	Geomean range	Chester et al. 1991	
North Atlantic		0.006–0.09	ng/m ³	Range	Smith and Carson 1981	
Baltic Sea, 1983		0.09, 0.01–0.43	ng/m ³	Mean, range	Hasanen et al. 1990	
Remote sites		0.001–0.9	ng/m ³	Range	Schroeder et al 1987	
<i>Ambient levels - rural/suburban/urban</i>						
Rural sites		0.08–10.1	ng/m ³	Range	Schroeder et al 1987	
Massachusetts, Nahant, 1992–1993		1.7	ng/m ³	Annual mean	Golomb et al. 1997	
Urban sites					Schroeder et al 1987	
United States		0.2–83	ng/m ³	Range		
Canada		1–7.9				
Europe		0.4–18.3				
Texas state average (1978–1982)		2.0	ng/m ³	Mean	Wiersema et al. 1984	
Illinois, urban air (<2.5 Fm; 2.5–10 Fm)					Sweet et al. 1993	
Bondville, Ill (rural)		Background	0.2; 0.1	ng/m ³	Mean (fine; coarse)	
Southeast Chicago		Steel mills	0.4; 0.4			
East St. Louis	Smelters	0.5; 0.4				
Washington, DC (1974)	Urban area	1.1	ng/m ³	Mean	Smith and Carson 1981	
<i>Ambient levels - industrial</i>						
Maryland, Baltimore Harbor Tunnel (1973–1974)					Ondov et al. 1982	
Air outside	Vehicular exhaust	0.8–1.9	ng/m ³	Range		
Air inside	Vehicular exhaust	2.2–5.3				
Ohio, Cleveland	Be-Cu alloy and other industrial activities	610	ng/m ³	Maximum	Smith and Carson 1981	

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Texas, El Paso Industrial 127 ng/m³ Maximum Wiersema et al. 1984
(1978–1982)

Table 6-2. Concentration of Cobalt in the Atmosphere (*continued*)

Location	Possible source/activity	Concentration ^a	Units	Type	Reference
Texas, Houston (1978–1982)	Urban area	81	ng/m ³	Maximum	Wiersema et al. 1984
Arizona, Tucson					Smith and Carson 1981
Urban	Copper smelting	1.9	ng/m ³	Mean	
Rural		0.7			
Maryland, Chalk Point Generator	Coal-burning power plant	3.86	ng/m ³	Mean	Smith and Carson 1981
Wales, Clydach	Nickel refining	48, 3–300	ng/m ³	Mean, range	Smith and Carson 1981
Wales, Llausamlet and Trebanos	Towns near Clydach	3.8		Mean	Smith and Carson 1981
<i>Occupational air levels</i>					
Northern Italy, exposure survey, 1991, area monitoring (n=259)	Diamond abrasive mfg.				Mosconi et al. 1994a
	Mould-filling	220, 47–960	ng/m ³	Median, range	
	Sintering	101.5, 32–240			
	Grinding	22, 15–45			
	Mechanical-working	20, 12–44			
	Grinding	5, 2.5–94			
	Tool production	6, 5–47			
	Hard metal alloy filing	2, 0.8–3			
	Other	2.7, 2.3–15			
Northern Italy, exposure survey, 1991, personal sampling (n=259)	Diamond abrasive mfg.				Mosconi et al. 1994a
	Mould-filling	382, 76–2,600	ng/m ³	Median, range	
	Sintering	309, 238–413			
	Grinding	230, 82–690			
	Mechanical-working	40, 7.1–65			
	Grinding	9.3, 1.5–178			
	Tool production	17, 4–28			

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Table 6-2. Concentration of Cobalt in the Atmosphere (*continued*)

Location	Possible source/activity	Concentration ^a	Units	Type	Reference
Japan, personal sampling, hard metal tool manufacture, 8-hour TWA, 356 workers (n=935)	Hard metal alloy filling	5, 1–107			Kumagai et al. 1996
	Other	50, 10–290			
	Powder preparation				
	rotation	459, 7–6,390	Fg/m ³	Mean, range	
	full-time	147, 26–378			
	Press				
	rubber	339, 48–2,910			
	steel	47, 6–248			
	Shaping	97, 4–1,160			
	Sintering	24, 1–145			
	Blasting	2, 1–4			
	Electron discharging	3, 1–23			
	Grinding	45, 1–482			

geomean = geometric mean; SD = standard deviation; TWA = time weighted average

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milling operations (Smith and Carson 1981). Eckel and Jacob (1988) analyzed U.S. Geological Survey (USGS) data for 6,805 ambient surface water stations and estimated the geometric mean and median dissolved cobalt concentration as 2.9 and 2.0 $\mu\text{g/L}$, respectively. Mean cobalt levels reported in seawater range from 0.078 $\mu\text{g/L}$ in the Caribbean Sea to 0.39 $\mu\text{g/L}$ in the Indian Ocean (Hamilton 1994). Vitamin B₁₂ is synthesized by bacteria, macrophytes, blue-green algae, and actinomycetes and cobalt levels in oceans often correlate with biological productivity. In the Baltic Sea, dissolved cobalt levels that are 1.0 ng/L near the surface, rise precipitously to 71.0 ng/L at a depth of 200 m (Brügmann 1988). The rise in dissolved cobalt is coincident with the onset of anoxic conditions and the presence of hydrogen sulfide, indicating that soluble bisulfide and polysulfide complexes may be present. Some cobalt levels reported in water are given in Table 6-3.

In a 1962–1967 survey, cobalt was detected in 2.8% of 1,577 U.S. raw surface waters from which drinking water is derived; the detection limit was 1 $\mu\text{g/L}$ and the maximum concentration was 48 $\mu\text{g/L}$ (NAS 1977). Of 380 U.S. finished drinking waters, only 0.5% contained cobalt levels exceeding 1 $\mu\text{g/L}$; the maximum concentration found was 29 $\mu\text{g/L}$ (NAS 1977). These values are higher than the respective median and maximum levels of <2.0 and 6.0 $\mu\text{g/L}$ found in Canadian finished drinking water (Meranger et al. 1981). Meranger et al. (1981) tested source water and drinking water in 71 municipalities across Canada and concluded that, in general, both surface water and groundwater used for drinking water supplies contain negligible amounts of cobalt. Greathouse and Craun (1978) analyzed 3,834 grab samples of household tap water from 35 geographical areas in the United States for 28 trace elements. Cobalt was found in 9.8% of the samples at concentrations ranging from 2.6 to 107 $\mu\text{g/L}$. It is not clear whether these higher levels could indicate that cobalt was picked up in the distribution system. In the earlier National Community Water Supply Study (2,500 samples), 62% of the samples contained <1 $\mu\text{g/L}$ Co/L; the average and maximum cobalt concentrations were 2.2 and 19 $\mu\text{g/L}$, respectively (Smith and Carson 1981). Cobalt was not detected (detection limit 8 $\mu\text{g/L}$) in a 1982–1983 survey of drinking water in Norway that covered 384 waterworks serving 70.9% of the Norwegian population (Flaten 1991).

The mean concentrations of cobalt in rain is around 0.03–1.7 $\mu\text{g/L}$ with levels generally ranging from 0.002 $\mu\text{g/L}$ at Enewetak Atoll to about 2.9 $\mu\text{g/L}$ in the Swansea Valley, Wales (Arimoto et al. 1985; Dasch and Wolff 1989; Hansson et al. 1988; Heaton et al. 1990; Helmers and Schrems 1995; Nimmo and Chester 1993; Nimmo and Fones 1997; Smith and Carson 1981). The highest recorded level of cobalt in precipitation was 68.9 $\mu\text{g/L}$ in the vicinity of a nickel smelter in Monchegorsk in the Russian Arctic (Reimann et al. 1997). An analysis of rain in the Mediterranean and urban and coastal sites in northwest

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Table 6-3. Cobalt Levels in Water

Nature/location of water	Level	Units	Type	Reference
<i>Sea water</i>				
Florida (Indian River Lagoon) (43 sites)	0.031, 0.006–0.050	µg/L	Mean, range	Trocine and Trefry 1996
California (Baja) 2–45 km offshore (n=11)	0.022–0.17	nM	Range	Sañudo-Wilhelmy and Flegal 1996
<100 m off shore (n=11)	0.11–0.59			
Agean Sea, 1994; 8 sites (dissolved)	0.168–0.632, 1.917	nM	Range of means, maximum	Voutsinou-Taliadouri 1997
Baltic Sea (Gotland Deep site)				Brügmann 1988
10 m	1.0	ng/L	Mean (dissolved Co)	
50 m	1.0			
100 m	3.5			
150 m	4.2			
200 m (anoxic)	71.0			
235 m (anoxic)	49.2			
Seawater background	0.04	µg/L		Bargagli 2000
Seawater	0.27	µg/L	Mean	Abbasi et al. 1989
<i>Fresh surface water</i>				
Freshwater background	0.05	µg/L		Bargagli 2000
U.S. ambient surface water (6,805 stations)	<2.9, 2.0	µg/L	Mean, median	Eckel and Jacob 1988
Five Great Lakes waters	ND–0.09	µg/L	Range	Rossmann and Barres 1988
Japan, unpolluted lake	<0.004	µg/L		Nojiri et al. 1985
Norway, 11 rivers	0.94	µg/L	Maximum	Flaten 1991
Streams near populated areas	1–10	µg/L	Range	Smith and Carson 1981
Streams in agricultural and mining areas	11–50	µg/L	Range	Smith and Carson 1981
Suspended solids in rivers	7–94	mg/kg	Range	Smith and Carson 1981
<i>Groundwater</i>				
Canada (Chalk River nuclear waste site)	0.0001–0.002	µg/L		Cassidy et al. 1982
Colorado (Denver) - shallow groundwater, (n=30)	<1 (<1–9)	µg/L	Median, range	Bruce and McMahon 1996

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Table 6-3. Cobalt Levels in Water (continued)

Nature/Location of water	Level	Units	Type	Reference
<i>Drinking water</i>				
Canadian drinking water (71 municipalities)				Meranger et al. 1981
Raw:	<2.0	µg/L	Median	
Treated:	<2.0			
Distributed:	#2.0			
<i>Precipitation</i>				
Massachusetts, 1984 (12 events)	0.045 (0.008), 0.02–0.12	µg/L	Mean (SD), range	Dasch and Wolff 1989
Rhode Island (rain/snow), 1985 (n=269)	0.038 (0.067)	ppb	Median (mean)	Heaton et al. 1990
	0.001–0.80		Range	
Western Mediterranean, 1988– 1989				Nimmo and Chester 1993
Total cobalt	0.029–0.134, 0.043	µg/L	Range, mean	
Labile cobalt	0.009–0.104, 0.025			
Organic cobalt	ND–0.613, 0.019			
Arctic (7 sites in Finland, Norway, Russia)	<0.02–1.07, 3.32	µg/L	Median range, maximum	Reimann et al. 1997
Russia (Monchegorsk), nickel smelter	11.8, 68.9		Median, maximum	

ND = not detected; SD = standard deviation

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England showed that about 33–44% of the cobalt occurred as very stable dissolved organic complexes (Nimmo and Chester 1993; Nimmo and Fones 1997).

As it was pointed out in Section 6.3.2.2, ^{60}Co discharged from the Steam Generating Heavy Water Reactor at Winfrith on the south coast of England was shown to be largely in the form of the nonionic trivalent complex, $^{60}\text{Co(III)}$ picolinate. The $^{60}\text{Co(III)}$ species is not immediately reduced to the more particle-reactive divalent form and both oxidation states may coexist for long periods of time in the environment. The proportion of the more soluble and mobile $^{60}\text{Co(III)}$ would be expected to increase with time and distance from the point of discharge. Shoreline water samples ($n=22$) taken in 1987–1988 at two locations in the vicinity of the discharge from the Steam Generating Heavy Water Reactor at Winfrith contained 0.3–16.2 mBq/L (8–437 fCi/L) of particulate ^{60}Co , 2.8–44.4 mBq/L (76–1,200 fCi/L) of soluble $^{60}\text{Co(II)}$, and 0.2–4.8 mBq/L (5–130 fCi/L) of soluble $^{60}\text{Co(III)}$ (Leonard et al. 1993). The percent of the soluble ^{60}Co present as Co(III) ranged from 4.3 to 18.6%. In 1989, in conjunction with the largest discharge of effluent from the plant, offshore seawater samples from 18 sites contained 0.06–2.22 mBq/L (fCi/L) of particulate ^{60}Co , 0.30–10.3 mBq/L (8.1–278 fCi/L) of soluble $^{60}\text{Co(II)}$, and 0.12–1.55 mBq/L (3.2–41.9 fCi/L) of soluble $^{60}\text{Co(III)}$. The percent of the soluble ^{60}Co present as Co(III) ranged from 6.0 to 28.6%.

6.4.3 Sediment and Soil

Cobalt is the 33rd most abundant element in the earth's crust. Its average concentrations in the earth's crust and in igneous rocks are 20–25 and 18 mg/kg, respectively (Abbasi et al. 1989; Merian 1985; Smith and Carson 1981). Trace metals in soils may originate from parent rock or from anthropogenic sources, primarily fertilizers, pesticides, and herbicides. Most soils contain 1–40 mg cobalt/kg. The average cobalt concentration in U.S. soils is 7.2 mg/kg (Smith and Carson 1981). Soils containing <0.5–3 mg cobalt/kg are considered cobalt-deficient because plants growing on them have insufficient cobalt (<0.08–0.1 mg/kg) to meet the dietary requirements of cattle and sheep. Cobalt-deficient soils include the humus podzols of the southeastern United States, and the podzols, brown podzolic soils, and humus groundwater podzols in the northeastern parts of the United States. The cobalt content of surface soils from 13 sites in the brown and dark brown soil zones of southwestern Saskatchewan ranged from 3.7 to 16.0 mg/kg and only in one case was the soil appreciably elevated above the corresponding parent material (Mermut et al. 1996). Fertilizers used in this agricultural area contained 0.12–102 mg Co/kg, median 5.7 mg/kg.

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Mean cobalt concentrations in surface soil from nine sites on two active volcanic islands off of Sicily ranged from 5.1 to 59.0 mg/kg (Bargagli et al. 1991). Soils near ore deposits, phosphate rocks, or ore smelting facilities, and soils contaminated by airport traffic, highway traffic, or other industrial pollution may contain much higher concentrations of cobalt; concentrations up to 800 mg/kg have been detected in such areas (Kloke et al. 1984; Smith and Carson 1981). Soils around the large copper-nickel smelters in Sudbury, Ontario have been shown to contain high levels of cobalt. Fifty kilometers from the smelters, cobalt levels in surface soil were 19 mg/kg. These levels increased to 48 mg/kg at 19 km, 33 mg/kg at 10 km and 42–154 mg/kg between 0.8 and 1.3 km from the smelter (Smith and Carson 1981). Soils around a cemented tungsten carbide tool grinding factory contained cobalt levels as high as 12,700 mg/kg, almost 2,000 times the average in U.S. soils (Abraham and Hunt 1995). However, neighborhood soils between 30 and 160 meters from the factory only contained 12–18 mg Co/kg.

Unpolluted freshwater sediment contains about the same levels of cobalt as does cobalt-sufficient soil, generally <20 mg/kg (Smith and Carson 1981). In the Hudson River Estuary, cobalt levels in suspended sediment was an order of magnitude higher than in bottom sediment (Gibbs 1994). This can be attributed to the finer grain size of suspended sediment or local sources. Cobalt levels in core samples (surface to 42 cm) from the Upper St. Lawrence Estuary were independent of depth indicating the lack of any recent significant anthropogenic releases (Coakley et al. 1993). Cobalt levels in sediment are shown in Table 6-4.

No broad-based monitoring studies of ^{60}Co or other radioactive cobalt isotopes in soil or sediment were found in the literature. Soil samples from the O-horizon taken from three sites in the 30-km zone around Chernobyl in 1992 and again in 1993, contained 14–290 and 4.5–245 Bq/kg (380–7,800 and 120–6,620 pCi/kg) dry weight of ^{60}Co , respectively (Lux et al. 1995). The Columbia River receives radiological contaminants along the Hanford Reach primarily through seepage of contaminated groundwater (PNNL 1996). The regional median concentration of ^{60}Co was highest along this reach. ^{60}Co activity in a sediment cores in water off of Southampton in southern England contained up to 28 Bq/kg (760 pCi/kg) in the upper 3 cm; no activity was found below 12.5 cm (Croudace and Cundy 1995). Discharges of treated effluent occurred on closing a steam generating heavy water reactor west of where the sampling was done. The maximum discharge occurred in 1980–1981.

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Table 6-4. Cobalt Levels in Sediment

Nature/location of sediment	Level	Units	Type	Reference
<i>Freshwater</i>				
Polluted lakes and rivers	0.16–133	mg/kg	Range	Smith and Carson 1981
Lake Ontario near Miesissauga, Canada	4.1–19.8	mg/kg	Range	Glooschenko et al. 1981
Hudson River, Foundry Cove, 1983, Ni-Cd battery plant, 1953–1979, Surficial (0–5 cm) sediment, 16 sites	18–700	mg/kg	Range	Knutson et al. 1987
<i>Estuaries and Marine</i>				
Hudson River Estuary (0–80 km from ocean), 1991				Gibbs 1994
Bottom sediment	1–13	mg/kg	Range	
Suspended sediment (near surface)	30–140			
Upper St. Lawrence Estuary, 1989–1990				Coakley et al. 1993
Core C168	3.1 (0.6)	mg/kg	Mean (SD)	
Cores LE and LO	2.7 (0.5)			
Massachusetts, New Bedford Harbor-core (0–25 cm)				Shine et al. 1995
Outer Harbor	7.03, 3.64–9.79	mg/kg	Mean, range	
Inner Harbor	6.38, 2.62–10.52			
Buzzards Bay (control site)	4.76, 1.64–8.19			
Indian River Lagoon, Florida (43 sites)	2.3, 0.4–6.3	mg/kg	Mean, range	Trocine and Trefry 1996
Gulf of Mexico				Villanueva and Botello 1998
Coastal areas (11 sites)	12.30–36.26	mg/kg	Range of means	
Continental shelf (3 sites)	6.39–21.00			
Antarctica (Ross Sea) continental shelf (n=12)	19, 0.10–13	mg/kg	Mean, range	Bargagli 2000
Northern Arctic Alaska, continental shelf (n=136)	9, 3.3–18	mg/kg	Mean, range	Bargagli 2000
Chukchi Sea, northeast Alaska (31 stations, surficial sediment)	32.7, 19–74	mg/kg	Mean, range	Naidu et al. 1997
Baltic Sea, southern, off Poland (surficial sediment)	0.69–18.10	mg/kg	Range	Szefer et al 1996
Baltic Sea (Gotland Deep site)	19, 11–33	mg/kg	Mean, range	Brügmann 1988

SD = standard deviation

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6.4.4 Other Environmental Media

The cobalt content of plants depends on the plant, the cobalt content of the soil and numerous environmental factors. The mean cobalt concentration reported for terrestrial plants was 0.48 µg/g, while the mean and median levels for freshwater vascular plants were 0.48 and 0.32 µg/g, respectively (Outridge and Noller 1991). The median cobalt level in freshwater vascular plants from polluted waters was about the same as in unpolluted waters, 0.37 µg/g, although extremely high levels of cobalt, up to 860 µg/g, was reported in one species, *Myriophyllum verticillatum*, from central Ontario lakes. Grasses normally contain 0.2–0.35 µg/g of cobalt, but grasses from cobalt deficient regions contain 0.02–0.06 µg/g of cobalt (Hamilton 1994). Durum wheat grown in southeastern Saskatchewan contained 0.01–0.02 mg/kg dry weight (Mermut et al. 1996). In view of the cobalt content of the soil and the fact that almost half of the cobalt in fertilizers used in the area was in a readily available form, the uptake of cobalt by wheat was negligible.

⁶⁰Co levels in plants and mushrooms in the 30-km zone around Chernobyl were mostly below the detection limit in samples obtained in 1992 and 1993; the highest activity recorded was 3.9 Bq/kg (110 pCi/kg) dry weight in *Athyrium filix femina* (Lux et al. 1995).

Eel and a freshwater fish from three Dutch polder lakes contained 2.5–25.0 and 2.50–5.63 mg cobalt/kg wet weight, respectively, (Badsha and Goldspink 1988). Ocean fish and rock crabs caught near dump sites off New York City, New Haven, Connecticut, and Delaware Bay contained 10–40 and 16.0 µg/kg, respectively in muscle tissue (Greig and Jones 1976). In a study of the levels and distribution of 14 elements in oceanic seabirds, the concentration of cobalt, an essential element, appeared to be highly regulated with over 80% of the body burden residing in the skeleton. The mean cobalt concentration in the livers of 11 seabird species ranged from 0.048 to 0.078 µg/g dry weight, and cobalt had the lowest coefficient of variation in the different species of the elements studied (Kim et al. 1998a). In another study in Antarctica, mean cobalt levels in fish and amphipods were 0.11–0.14 and 1.01 µg/g dry weight, respectively, while those in the tissue of penguin and other sea birds ranged from 0.09 to 0.11 µg/g (Szefer et al. 1993). The concentration of cobalt in the tissue of 14 bluefin tuna caught by various commercial fishing vessels off Newfoundland was essentially the same, 0.01±0.004 µg/g (Hellou et al. 1992a). Similarly, in a broad survey of contaminant levels in nine species of fish and fiddler crabs from 11 sites in the lower Savannah River, Georgia and the Savannah National Wildlife Refuge, mean cobalt levels among different species and sites were statistically indistinguishable (Winger et al. 1990). These

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and other studies indicate that cobalt does not biomagnify up the food chain (Smith and Carson 1981). While cobalt was found in high levels in sediment from the Tigris River in Turkey and in low levels in the water, it was not detected in two species of fish (Gümüş et al. 1994).

Some female birds sequester metals into their eggs under certain conditions, a phenomenon that may jeopardize the developing embryos. The geometric mean concentrations of cobalt in tern eggs collected from coastal New Jersey in 1971 and 1982 were 0.48 and 0.50 mg/kg, respectively. Unlike the levels of seven other common metals (e.g., mercury, cadmium, copper, lead, manganese, nickel, and zinc), the level of cobalt in tern eggs (and in the environment) showed no decline over the 11-year period (Burger and Gochfeld 1988).

Table 6-5 shows the levels of cobalt in foods items and food categories from different countries. The level of cobalt in most Canadian foods was low; items with the highest concentrations were waffles (76 ng/g), corn cereal (74 ng/g), and potato chips (70 ng/g) (Barceloux 1999; Dabeka and McKenzie 1995). Green leafy vegetables and fresh cereals are the richest sources of cobalt (0.2–0.6 µg/g dry weight), while dairy products, refined cereals, and sugar contain the least cobalt (0.1–0.3 µg/g dry weight). The levels of cobalt were determined in 50 different food items, mainly meat, fish, fruit, vegetables, pulses, and cereals on the Swedish market during the years 1983–1990 (Jorhem and Sundström 1993). Beef liver and seeds were fairly high in cobalt and fish, fruit, and root and leafy vegetables were under 0.01 mg cobalt/kg fresh weight. The cobalt levels in mg/kg fresh weight were highest in alfalfa seeds, 0.86; linseed, 0.56; milk chocolate, 0.34; dark chocolate, 0.24; white poppy seeds, 0.30; blue poppy seeds, 0.15; soya beans, 0.084; green lentils, 0.054; and beef liver, 0.043. The cobalt content of 20 brands of alcoholic and nonalcoholic beer widely consumed in Spain ranged from 0.16 to 0.56 µg/L with a median of 0.39 µg/L (Cameán et al. 1998). Cobalt, which was at one time added to beer to increase the foam head, has been associated with cardiomyopathies in heavy beer drinkers.

Cobalt is present in various consumer products including cleaners, detergents, and soaps, which have resulted in dermatitis in sensitive individuals (Kokelj et al. 1994; Vilaplana et al. 1987). Tobacco contains about <0.3–2.3 µg Co/g dry weight and approximately 0.5% of the cobalt appears in mainstream smoke (Barceloux 1999; Munita and Mazzilli 1986; Ostapczuk et al. 1987; Stebbens et al. 1992).

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Table 6-5. Cobalt Levels in Food

Food item	Level	Units ^a	Type	Reference
<i>Infant formulas/milk</i>				
Evaporated milk (n=21)	0.74, 0.52–2.6	µg/kg ^b	Median, range	Dabeka 1989
Ready-to-use formula (n=49)	0.53, 0.21–5.2	µg/kg ^b	Median, range	Dabeka 1989
Milk-based (n=33)	0.40, 0.21–0.99			
No added iron (n=6)	0.36, 0.21–0.61			
Added iron (n=27)	0.87, 0.41–0.99			
Soy-based (n=16)	2.27, 1.71–5.2			
Concentrated liquid formula (n=50)	2.27, 0.25–11.8	µg/kg ^b	Median, range	Dabeka 1989
Milk-based (n=34)	1.57, 0.25–3.11			
No added iron (n=20)	1.06, 0.25–1.77			
Added iron (n=14)	2.59, 2.03–3.11			
Soy-based (n=16)	4.33, 2.7–11.8			
Powdered formula (n=64)	9.54, 2.6–53	µg/kg ^b	Median, range	Dabeka 1989
Milk-based (n=36)	4.96, 2.6–10.6			
No added iron (n=23)	4.24, 2.6–9.6			
Added iron (n=13)	8.26, 5.1–10.6			
Soy-based (n=28)	20.0, 10.6–53			
<i>Agricultural crops</i>				
Cabbage, United States	0.2	mg/kg ^c	Typical level	NAS 1977
Corn seed, United States	0.01	mg/kg ^c	Typical level	NAS 1977
Fruits, 12 types, Poland	0.01–0.02	mg/kg	Range	Bulinski et al. 1986
Lettuce, Sweden 1983–1990 (n=7)	0.002, 0.006	mg/kg	Mean, maximum	Jorhem and Sundström 1993
Lettuce, United States	0.2	mg/kg ^c	Typical level	NAS 1977
Onions, 11 Danish sites (n=110)	1.51, 0.119–5.1	µg/kg	Median, range	Bibak et al. 1998a
Peas, 10 Danish sites (n=93)	4.6, 0.57–17	µg/kg	Median, range	Bibak et al. 1998b
Potatoes, Sweden (n=8)	0.008, 0.017	mg/kg	Mean, maximum	Jorhem and Sundström 1993
Spinach, United States	0.4–0.6	mg/kg ^c	Typical range	NAS 1977
Strawberries, Sweden (n=10)	0.004, 0.010	mg/kg	Mean, maximum	Jorhem and Sundström 1993
Vegetables, 30 types, Poland	0.008–0.032	mg/kg	Range	Bulinski et al. 1986
White flour, United States	0.003	mg/kg ^c	Typical level	NAS 1977

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Table 6-5. Cobalt Levels in Food (*continued*)

Food item	Level	Units ^a	Type	Reference
<i>Meat, fish, beverages</i>				
Beef, Sweden (n=3)	0.001, 0.001	mg/kg	Range, maximum	Jorhem and Sundström 1993
Beef liver, Sweden (n=3)	0.043, 0.074	mg/kg	Range, maximum	Jorhem and Sundström 1993
Beef kidney, Sweden (n=3)	0.008, 0.010	mg/kg	Range, maximum	Jorhem and Sundström 1993
Beer, Spain, 20 brands	0.39, 0.16–0.56	Fg/L	Median, range	Cameán et al. 1998
Cocoa, Germany	1.31	mg/kg ^c		Ostapczuk et al. 1987
Coffee (whole), South Africa	0.93	mg/kg ^c		Horwitz and Van der Linden 1974
Coffee (whole), Germany (61% water extractable)	0.11–0.31	mg/kg ^c	Range	Ostapczuk et al. 1987
Fish, Sweden, 10 varieties (n=40)	<0.001–.008, 0.020	mg/kg	Range of mean, maximum	Jorhem and Sundström 1993
Pork, Sweden (n=36)	0.001, 0.012	mg/kg	Range, maximum	Jorhem and Sundström 1993
Pork liver, Sweden (n=36)	0.010, 0.023	mg/kg	Range, maximum	Jorhem and Sundström 1993
Pork kidney, Sweden (n=36)	0.004, 0.011	mg/kg	Range, maximum	Jorhem and Sundström 1993
Tea (whole), South Africa	0.2	mg/kg ^c		Horwitz and Van der Linden 1974
Tea (whole), Germany (40% water extractable)	0.18–6.7	mg/kg ^c	Range	Ostapczuk et al. 1987
<i>Food categories</i>				
Bakery good/ cereals, Canada (n=24)	10.9, 75.7	µg/kg	Median, maximum	Dakeba and McKenzie 1995
Beverages, Canada (n=7)	5.9, 9.1	µg/kg	Median, maximum	Dakeba and McKenzie 1995
Fats and oils, Canada (n=3)	<2.6, 37.6	µg/kg	Median, maximum	Dakeba and McKenzie 1995
Fish, Canada (n=6)	18.6, 14.3–29.4	µg/kg	Median, range	Dakeba and McKenzie 1995
Fruits and fruit juices, Canada (n=25)	<6.6, 35.7	µg/kg	Median, maximum	Dakeba and McKenzie 1995
Meat and poultry, Canada (n=18)	<5.5, 38.2	µg/kg	Median, maximum	Dakeba and McKenzie 1995

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Table 6-5. Cobalt Levels in Food (*continued*)

Food item	Level	Units ^a	Type	Reference
Milk and milk products, Canada (n=13)	<1.4, 18.9	µg/kg	Median, maximum	Dakeba and McKenzie 1995
Soups, Canada (n=4)	5.6, 8.5	µg/kg	Median, maximum	Dakeba and McKenzie 1995
Sugar and candy, Canada (n=7)	<0.4, 3.5	µg/kg	Median, maximum	Dakeba and McKenzie 1995
Vegetables, Canada (n=38)	2.4, 18.1	µg/kg	Median, maximum	Dakeba and McKenzie 1995

^aproduce on a fresh weight basis, unless otherwise specified.^bas sold^cdry weight basis

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Table 6-6. Cobalt Content of Miscellaneous Substances

Substance/source	Level	Units	Type	Reference
Bituminous coal used for power generation	6.4	mg/kg	Median	Rubin 1999
Coal, United States	~5	mg/kg	Mean	Smith and Carson 1981
Fly ash	~25	mg/kg	Mean	Smith and Carson 1981
MSW Incinerator ash, Mississippi				Buchholz and Landsberger 1995
Fly ash (n=30)	11.3–13.5	Fg/g	Range	
Bottom ash (n=30)	65.2–90.3			
Combined ash (n=30)	24.8–30.5			
MSW Incinerator ash, United States, 1987				Mumma et al. 1990
Fly ash (n=5)	18.2–54.0	Fg/g	Range	
Bottom ash (n=7)	13.5–35.1			
Combined ash (n=8)	11.2–43.4			
Compost, Toronto				Evans and Tan 1998
Residential compost	8.1, 3.2–12	mg/kg	Median, range	
Greenhouse finished compost	6.1±1.03		Mean ± SD	
Sewage sludge				
16 large U.S. cities	11.3, 6.08–29.1	mg/kg	Median, range	Gutenmann et al 1994
32 U.S. cities	7.2, 2.4–30.1	mg/kg	Median, range	Mumma et al. 1984
Cow manure (comparison)	6.1	mg/kg		Mumma et al. 1984
Miscellaneous soil amendments ^a				Raven and Loeppert 1997
Compost	3.55, 3.57	mg/kg	Individual means	
Diammonium phosphate	3.24, 0.68			
Dolomite	0.33			
Manure	2.23			
Monoammonium phosphate	0.78, 3.38			
Rock phosphate, Tilemsi	19.6			
Rock phosphate, North Carolina	<0.08			
Sewage sludge, Austinite	4.10			
Sewage sludge, Milorganite	4.07			
Triple superphosphate	6.61, 2.24			
Street dust, New York City	8.7–12.9	µg/g	Range	Fergusson and Ryan 1984

^aThe rest of the 24 fertilizers and soil amendments tested were below the detection limit (typically <0.07 ppm).

MSW = municipal solid waste; SD = standard deviation

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The cobalt content of sewage sludge, incinerator ash, fertilizers, soil amendments, and other substances appears in Table 6-6. The concentration of cobalt in U.S. coal averages about 5 mg/kg, levels in crude oil and fuel oil ranges from 0.001 to 10 and 0.03 to 0.3 mg/kg and those in gasoline are <0.1 mg/kg (Smith and Carson 1981). Cobalt levels were below the detection limit of 0.05 ppm dry weight in all but 1 of 26 samples of composted yard waste, sewage sludge, and municipal solid waste samples nationwide in 1991. The one positive sample of composted yard waste contained 1.53 ppm of cobalt (Lisk et al. 1992).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Exposure of the general population to cobalt occurs through inhalation of ambient air and ingestion of food and drinking water. In general, exposure from food is much greater than from drinking water, which in turn, is much greater than from air. From the limited monitoring data available, the average concentration of cobalt in ambient air in the United States is approximately 0.4 ng/m³. However, levels may be orders of magnitude higher in source areas. Therefore, exposure to cobalt in air will vary substantially from nonsource areas to areas with cobalt-related industries. Similarly, the median cobalt concentration in U.S. drinking water is <2.0 µg/L; however, values as high as 107 µg/L have been reported in surveys of water supplies (Smith and Carson 1981). Therefore, exposure from drinking water may vary considerably from one location to another. In Canada, the daily cobalt intake of the average adult from drinking water is #2.6 µg; this could increase to 10 µg for those living in areas with the highest cobalt levels (Meranger et al. 1981).

General population exposure to cobalt from food is highly variable and normally higher than intake from drinking water. Most of the cobalt ingested is inorganic; vitamin B₁₂, which occurs almost entirely in food of animal origin, constitutes only a very small fraction of cobalt intake. The cobalt intake in food has been estimated to be 5.0–40.0 µg/day (Jenkins 1980). The daily cobalt intake, including food, water, and beverages of two men that were followed for 50 weeks was much higher, 310 and 470 µg (Smith and Carson 1981). The estimated average daily cobalt intake from diet in Canada was 11 µg/day; the intake varied between 4 and 15 µg/day between the various age/sex groups (see Table 6-7) (Barceloux 1999; Dabeka and McKenzie 1995). The contributions of various food groups to cobalt intake in this study were (category, contribution of dietary intake): bakery goods and cereals, 29.8%; vegetables, 21.9%; beverages, 9.8%; milk and milk products, 9.4%; meat and poultry, 9.1%; soups, 6.4%; fruit and fruit juices, 5.0%; sugar and candies, 2.8%; fish, 2.7%; fats and oils, 2.2%; and miscellaneous, 1.1%. The

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Table 6-7. Mean Daily Dietary Intake of Cobalt for Selected Population Groups in Canada

Group	Mean daily intake (µg/day)
1–4 years	7
5–11 years	10
12–19 years; male	14
12–19 years; female	10
20–39 years; male	15
20–39 years; female	9
40–65 years; male	12
40–65 years; female	9
65+; male	10
65+; female	8

Source: Dabeka and McKenzie 1995

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average daily intakes of cobalt in France was estimated to be 29 µg/day (Biego et al. 1998). In this study, foods were divided into nine categories. The foods accounting for the greatest contributions of cobalt intake were milk and dairy products, fish-crustaceans, and condiments-sugar oil, respectively contributing 32, 20, and 16% to the daily intake. The U.S. Department of Agriculture (USDA) conducted a special exploratory study in 1985–1986 to determine the concentration of trace metals in tissue of health livestock and poultry randomly selected from those slaughtered. Between 0.6 and 5.9% of samples in the 11 production classes had levels of cobalt that exceeded the lowest reliable quantitation level of 0.15 ppm and the mean of positive samples ranged from 0.20 to 0.23 ppm in all classes but heifer/steer, which had a level of 1.92 ppm (Coleman et al. 1992). Cobalt, which has been added to beer to increase the foam head, has been associated with cardiomyopathies in heavy beer drinkers. However, according to a recent Spanish study, the low levels of cobalt presently found in beer do not make a significant contribution to the total cobalt intake in heavy beer drinkers (Cameán et al. 1998). Smokers may be exposed to cobalt in mainstream smoke, but the level of exposure has not been assessed (Barceloux 1999).

Since cobalt and other heavy metals have been used on hand painted china, a study was conducted to see whether these metals are released into food under acidic conditions. Forty-six samples of porcelain dinnerware from Europe or Asia that was manufactured before the mid-1970s and had hand-painted designs over the glaze was filled with 4% acetic acid to within 7 mm of the rim and analyzed after 24 hours (Sheets 1998). Of these, 36 samples released <0.02 µg/mL of cobalt and 10 released 0.020–2.9 µg/mL. The Food and Drug Administration (FDA) has not established dinnerware extraction limits for cobalt.

Data are lacking on the levels of cobalt in tissues and fluids of the general populations in the United States; values from various countries are given in Table 6-8. As can be seen from this table, cobalt concentrations are greatest in nail, hair, and bone. The differences in cobalt levels in similar human tissues (e.g., hair, nail) in different countries may be due to differences in dietary and living habits and levels of cobalt in food (Takagi et al. 1988). The total amount of cobalt in the body of an adult as vitamin B₁₂ is about 0.25 mg, of which 50–90% is contained in the liver (IARC 1991).

Surgical implants for knee and hip replacements often use cobalt-containing alloys which may lead to elevated cobalt levels in body fluids. Indeed, cobalt levels in serum and urine have been used as an index

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Table 6-8. Cobalt Levels in Human Tissues and Fluids

Tissue or fluid	Level	Units ^a	Type	Reference
Urine, U.S., NHANES, representative population (n=1007)	0.36, 0.11–0.89	µg/L	Geomean, 10 th –90 th percentile	CDC 2001
Urine, The Netherlands	<0.2–1.2	µg/L	Range	Bouman et al. 1986
Urine, Sweden	0.5, 0.1–2.2	µg/L	Mean, range	Alexandersson 1988
Urine, Denmark (3 reference groups)				Poulsen et al 1994
Unexposed control females (n=46)	1.5, LOD–20.5	nmol ^b	Mean, range	
Unexposed males (n=12)	0.9, LOD–2.31			
Unexposed females (n=11)	5.9, LOD–25.02			
Urine, hip arthroplasty patients, observed 7–15 years (n=17)	0.9–1.05	µg/L	Range	IARC 1991
Urine, hip arthroplasty patients, observed 5–15.5 years (n=10)	3.8	µg/L	Mean	IARC 1991
Urine, 48 metal sharpening workers in 12 Italian factories	0–40.3, 86	µg/L	Range of means, maximum	Imbrogno et al. 1994
Urine, 12 female cobalt powder sintering workers, Italy				Ferdenzi et al. 1994
Monday, before shift	25, 1–51	µg/L	Mean, range	
Friday, before shift	29, 3–159			
Friday, end-of shift	85, 6–505			
After 3-week holiday	11, 4–34			
Urine, Italian workers wet grinding of hard metal tools (end of shift)				Sesana et al. 1994
Factory A no local exhausts (n=3)	138.3 (108), 123.7 (74)	µg/L	Mean (SD) Monday, Friday	
Factory B local exhausts (n=5)	15.3 (7.7), 24.4 (14.1)			
Factory C local exhausts (n=3)	48.2 (7.3), 74.7 (13)			
Urine, Northern Italy, 1991, occupational exposure survey, 314 exposed people				Mosconi et al. 1994
Diamond abrasive production				
Mould-filling	320, 587, 39–2,100	µg/L	Median, mean, range	
Sintering	168, 193, 102–390			
Grinding	61, 151, 34–520			
Mechanical-working	50, 67, 143–165			
Grinding	15, 32. 0.8–730			
Tool production	12, 19, 0.8–100			

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Hard metal alloy filling 5, 5, 0.8–18
 Other 1, 2.9, 0.8–72

Table 6-8. Cobalt Levels in Human Tissues and Fluids (*continued*)

Tissue or fluid	Level	Units ^a	Type	Reference
Blood, Denmark, porcelain factory				Raffn et al. 1988
Plate painters, off work for 6 weeks (n=46)	8.05, 1.70–22.1	nmol/L	Mean, range	
Plate painters, working 4 weeks (n=46)	36.7, 3.40–407			
Top glaze painters (unexposed) (n=51)	4.04, <1.70–10.2			
Urine, Denmark, porcelain factory				Raffn et al. 1988
Plate painters, off work for 6 weeks (n=46)	81.8, <1.70–445	nmol/L	Mean, range	
Plate painters, working 4 weeks (n=46)	1,308, 37.4–14,397			
Top glaze painters (unexposed) (n=51)	16.0, <1.70–234			
Plasma, Sweden	0.1–1.2	µg/L	Range	Alexandersson 1988
Whole Blood, Denmark (3 Reference groups)				Poulsen et al 1994
Unexposed control females (n=46)	4.1, <1.7–10.2	nmol/L	Mean, range	
Unexposed males (n=12)	3.1, <1.7–6.8			
Unexposed females (n=11)	7.6, <1.7–30.5			
Lung, Sweden				Gerhardsson et al. 1988
rural	0.007	mg/kg	Mean	
urban	0.011			
Liver, New Zealand (n=96)	0.120	mg/kg	Mean	IARC 1991
Tissue, Japan				Yamagata et al. 1962
Pectoral muscle	0.016	mg/kg	Mean	
Rib bone	0.036			
Stomach	0.021			
Liver	0.017			
Brain	0.0055			
Urinary bladder	0.0055			
Kidney	0.012			
Aorta	0.021			
Nails				Takagi et al. 1988
Canada (n=40)	0.09	mg/kg	Mean	
India (n=100)	0.06			
Japan (n=252)	0.17			

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Table 6-8. Cobalt Levels in Human Tissues and Fluids (*continued*)

Tissue or fluid	Level	Units ^a	Type	Reference
Poland (n=49)	0.04			
U.S. (n=71)	0.06			
Adipose tissue	0.035–0.078	mg/kg	Range	EPA 1986
Hair				Takagi et al. 1986
Canada (n=92)	0.043	mg/kg	Mean	
India (n=255)	0.051			
Japan (n=457)	0.18			
Poland (n=46)	0.022			
United States (n=55)	0.047			
Hair, Italy				Vienna et al. 1995
Male biology students (n=20)	0.007, 0.001–0.07	mg/kg	Geomean, range	
Female biology students (n=20)	0.017, 0.001–0.28			
Hair, Pakistan				Ashraf et al 1995
rural (n=28)	2.05, 0.10–4.80	mg/kg	Mean, range	
urban (n=39)	3.86, 1.10–5.90			

^afresh weight, unless otherwise specified^bcreatinine basis

geomean = geometric mean; NHANES = Nation Health and Nutrition Examination Survey; SD = standard deviation

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of prosthesis wear. In some cases, significant increases in cobalt levels have been observed, while in other cases, elevations were much lower or only sporadic (IARC 1991). These differences have been ascribed to greater release rates from metal to metal than metal to polyethylene articular surfaces as well to differences in the cobalt-containing alloys.

There are several reports of cobalt exposure among occupational groups. The concentrations of cobalt in the air of hard metal manufacturing, welding, and grinding factories may range from 1 to 300 $\mu\text{g}/\text{m}^3$, compared to normal atmospheric levels of 0.4–2.0 ng/m^3 (Burr and Sinks 1989; Haddad and Zikovsky 1985; Koponen et al. 1982; Lichtenstein et al. 1975). The maximum OSHA permissible level is 100 $\mu\text{g}/\text{m}^3$. The concentration of cobalt in the dust of an electric welding factory was 4.2 $\mu\text{g}/\text{g}$ compared to its normal dust level of 0.1–1.0 $\mu\text{g}/\text{g}$ (Baumgardt et al. 1986). The higher rate of exposure to cobalt for occupational groups is also reflected in the higher cobalt content in tissues and body fluids of living and deceased workers in this group. The levels of cobalt in the urine of workers in the hard metal industry varied with the levels of cobalt concentration in the working atmosphere. At a concentration of 0.09 mg/m^3 , the urinary excretion of cobalt exceeded normal values by orders of magnitude. When the cobalt concentration in the working atmosphere was 0.01 mg/m^3 or lower, urinary cobalt excretion was 4–10 times higher than normal level (Alexandersson 1988; Scansetti et al. 1985). At high exposure levels, the cobalt concentration in blood was 20 times higher than normal; in the low exposure group, it was only slightly higher than in the control group (Alexandersson 1988).

An extensive survey of workers potentially exposed to cobalt in the Bergamo Province in northern Italy in 1991 identified 403 exposed workers in different production areas (Mosconi et al. 1994a). Significant cobalt exposure occurred especially for operators working in diamond abrasive production, and in particular, in mould filling and sintering units where environmental limits are regularly exceeded. Exposure in tool production, tool sharpening, and hard metal alloy filling is much more restrained. Occupational cobalt air levels and urinary excretion levels recorded in the survey appear in Tables 6-2 and 6-8.

In the hard metal industry in Japan, Kumagai et al. (1996) found that mean 8-hour time weighted averages (TWAs) were $>50 \mu\text{g}/\text{m}^3$ for workers involved in powder preparation (rotation), powder preparation (full-time), rubber press, and shaping operations; mean exposure levels were 459, 147, 339, and 97 $\mu\text{g}/\text{m}^3$, respectively. Workers involved in the manufacture and maintenance of hard metal and stellite blades in Finland were exposed to breathing zone cobalt concentrations ranging from 0.002 to 0.240 mg/m^3 , with a

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geometric mean of 0.017 mg/m^3 (Linnainmaa et al. 1996). The average proportion of water soluble cobalt in airborne cobalt was 68% (range 14–100%). Wet grinding was not sufficient to adequately control cobalt levels and coolant cobalt levels were high. In a group of 12 factories in Italy in which 48 workers were tested who were exposed to cobalt in operations such as sharpening with diamond grinding stones, the mean concentration of cobalt in air was 21.2 and $137.7 \text{ } \mu\text{g/m}^3$ (PEL-TWA $100 \text{ } \mu\text{g/m}^3$) in work places with and without dust ventilation, respectively (Imbrogno et al. 1994).

Ferdenzi et al. (1994) obtained a correlation between Friday TWA air cobalt levels and Friday end-of-shift urine levels among women in the powder sintering industry. The mean urine cobalt level in the factories ranged from 0 to $40.3 \text{ } \mu\text{g/L}$ and the maximum was $86 \text{ } \mu\text{g/L}$. The average urinary cobalt level among workers using wet/mixed sharpening methods was 4 times higher than those using dry sharpening methods. Cobalt urine levels increased rapidly during a shift and dropped significantly overnight and after a weekend. Gallorini et al. (1994) found that the ratio of inorganic to organic cobalt in the urine of hard metal workers was 2.3 compared to 1.01 in controls; the ratio was constant over the range of urinary cobalt levels analyzed ($180\text{--}1,254 \text{ } \mu\text{g/L}$). Exposure to cobalt during the wet grinding of hard metal tools (Widia tools) used in the wood industry produced exposure to cobalt above the PEL-TWA of $100 \text{ } \mu\text{g/m}^3$ (Sesana et al. 1994). However, exhausts near the grinding wheels were shown to substantially reduce exposure levels (see Table 6-8). In the processing department of a small company producing carbide tip saw blades for the woodworking industry, area air sampling showed that exposure levels were low in all departments except tip grinding where wet and dry tip grinding areas contained 55 and $21 \text{ } \mu\text{g/m}^3$ of cobalt, respectively (Stebbins et al. 1992). Respirable cobalt levels ranged from 2 to $28 \text{ } \mu\text{g/m}^3$. Wet grinding is a traditional method for controlling dust during grinding. However, some coolants may contain significant concentrations of cobalt (in this case, $61\text{--}538 \text{ mg/mL}$) that can contribute to exposure during grinding. Among cobalt blue dye plate painters in a porcelain factory in Denmark, the blood and urine cobalt levels were, respectively, 2–4 and 5–15 times higher than in control groups (Raffn et al. 1988). Similarly, lungs taken from deceased, occupationally exposed workers also had higher levels of cobalt than lungs from control groups. Lungs of deceased hard metal industry workers in Sweden contained 2.5–4 times higher levels of cobalt than control lungs (Gerhardsson et al. 1988). Similarly, the lungs of coal miners from England contained 6 times higher cobalt levels than control lungs (Hewitt 1988).

Workers at nuclear facilities, irradiation facilities, or nuclear waste storage sites may be accidentally exposed to radioisotopes of cobalt. Also, workers using cobalt isotopes in tracer studies, in calibration or

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other devices, or ^{57}Co in Mössbauer spectroscopy, may be exposed to radiocobalt. Exposure would generally be to radiation produced by these isotopes (e.g., gamma radiation from ^{60}Co). Patients receiving ^{60}Co radiotherapy will obviously be exposed to its radiation. According to the NRC (1999), the collective intake of ^{60}Co by ingestion and inhalation at power reactors in 1998 was 352 μCi (13 MBq) for 25 intake records and 27,000 μCi (1,000 MBq) for 281 intake records (NRC 1999). The collective intake at fuel fabrication facilities was 0.486 μCi (0.180 MBq) for 502 intake records.

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

As with adults, most children are exposed to cobalt largely through their diet. Dabeka and McKenzie (1995) estimated that the dietary cobalt intake by Canadian children ages 1–19 ranged from 7 to 14 mg/day (see Table 6-7). Milk constitutes a larger part of children's diets than that of adults, and infants may consume infant formula. Cow's milk contains 0.3–0.8 ng/g cobalt (Dakeba 1989). The levels of cobalt in human milk from Nigeria, Zaire, Guatemala, Hungary, Philippines, and Sweden ranged from 0.15 (Hungary) to 1.4 $\mu\text{g/g}$ (Philippines), median 0.32 $\mu\text{g/g}$ (Nriagru 1992). Garg et al. (1993) reported much lower cobalt levels in three samples of human milk in India, 2.42 ng/g, and 5.07 ng/g in cow's milk. Dakeba (1989) determined cobalt levels in various infant formulas (see Table 6-5). Milk-based infant formulas and evaporated milk contained <1 ng/g of cobalt on a "ready-to-use" basis. Milk-based formulas with added iron contained about twice those with no added iron and soy-based formulas contained about 5 times more. The influence of added iron suggests that the cobalt in formula is not primarily from vitamin B₁₂. Using literature values of cobalt in food, Dakeba also estimated that infants

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0–12 months old ingest an average of 0.52 µg Co/kg-day (3.93 µg/day) from food and water and that for an infant, 0–12 months old, the total dietary cobalt intake would range from 0.42 µg/kg-day (3.39 µg/day) for a breast or milk-based formula fed infant to 1.0 µg/kg-day (7.33 µg/day) for an infant fed soy-based formula powder. The recommended dietary allowance for Canadian infants is 0.012 µg/day cobalt as vitamin B₁₂. In a 1967 study of the total dietary intake of some trace elements, excluding drinking water, of institutionalized children aged 9–12 in 28 U.S. cities, cobalt intake ranged from 0.297 to 1.767 mg/day with a mean value of 1.024 mg/day (Murthy et al. 1971).

Cobalt exposure in communities near mining and smelting facilities or metal shops where cobalt is used in grinding tools are a public health concern, especially for infants and children. Since cobalt remains in the surface soil indefinitely and long past land uses may be forgotten, people may not realize that they are living in areas where high levels of cobalt may occur in soil. Contaminated soils pose a particular hazard to children because of both hand-to-mouth behavior and intentional ingestion of soil (pica) that contain metals and other contaminants (Hamel et al. 1998). In these communities, cobalt may have been tracked in from outdoors and contaminate carpeting. Cobalt-containing dust may be brought home in the clothing of parents working in industries where they are exposed to cobalt. Children may be exposed to this cobalt while crawling around or playing on contaminated carpeting. Exposure may also result from dermal contact with soil, or by inhaling dust and then swallowing it after mucociliary transport up out of the lungs. Because there is little absorption of cobalt through the skin following dermal exposure, and because much of the cobalt in soil is embedded in or adsorbed to soil particles or insoluble, it may not be in a form accessible for uptake by the body, and therefore may not pose a serious health hazard.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to workers in the hard metal industry (tool production, grinding, etc.) and industries such as coal mining, metal mining, smelting and refining, cobalt dye painters, and the cobalt chemical production, the general population living near these industries may be exposed to high levels of cobalt in air and in soil. Exposure to cobalt during the wet grinding of hard metal tools is especially high when local exhausts are not in use (Sesana et al. 1994). People living near hazardous waste sites may be exposed to cobalt by inhaling dust from contaminated sites or through dermal contact with cobalt-contaminated soil. In the case of children playing in and around unrestricted landfill sites, exposure via dermal and ingestion routes is possible. The general populations in agricultural areas that use sewage sludge or cobalt-containing fertilizers or other soil amendments may be exposed to higher levels of cobalt via inhalation of

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dust or dermal contact with the soil. However, no experimental evidence of higher than normal exposures for these population groups was found in the literature. People who live in areas that naturally contain higher levels of cobalt minerals may also be exposed to higher levels of cobalt from both the inhalation and dermal contact routes.

The higher exposure of cobalt in patients with cobalt-chromium knee implants has been demonstrated by the slightly higher levels of cobalt in whole blood, serum, and urine, and by very high levels of cobalt in bone of these patients (IARC 1991; Ostapczuk et al. 1985; Sunderman et al. 1989). Prosthetic devices that contain polyethylene components to avoid metal-to-metal contact do not appear to cause elevated levels of cobalt in tissues and body fluids (IARC 1991; Ostapczuk et al. 1985; Sunderman et al. 1989). People who use cobalt supplements as a treatment for anemia and those who take large amounts of vitamin B-12 as a dietary supplement would have higher intakes of cobalt than the general population.

Workers at nuclear facilities and nuclear waste storage sites may be exposed to potentially high levels of radiation exposure from ^{60}Co and ^{58}Co . Workers at irradiation facilities using ^{60}Co may be exposed to potentially high levels of gamma radiation exposure from this isotope. Patients receiving ^{60}Co radiotherapy will intentionally be exposed to high levels of gamma radiation.

6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of cobalt is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of cobalt.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

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6.8.1 Identification of Data Needs

Physical, Chemical and Radiological Properties. As can be seen from Table 4-2 and Section 4.2, the relevant physical and chemical properties of cobalt and its compounds are sufficiently known to enable prediction of environmental fate and transport of cobalt compounds (Budavari 1996; Lide 1994; Stokinger 1981; Weast 1985). Information on the radiological properties of important cobalt isotopes are also well known (see Table 4-3) (ICRP 1983, Lide 1994).

Production, Import/Export, Use, Release, and Disposal. Information on the production, import/export, use, release, and disposal of a chemical is important because it is an indicator of possible environmental contamination and human exposure. Large releases and consumer use would indicate higher general population exposure from environmental sources (e.g., air, drinking water, and food) and use of consumer products. Occupational exposure may also increase with increased production and use. U.S. production of cobalt is derived primarily from scrap (secondary production). Information is available on cobalt consumption derived from secondary production, import/export, and release of cobalt from the National Defense Stockpile (USGS 1998, 1999). However, production volumes of individual cobalt compounds are not available. Information on the production of individual compounds would be useful in assessing exposure to specific cobalt compounds. Cobalt isotopes, primarily ^{60}Co and ^{57}Co , are not commercially produced in the United States, but rather are imported from Canada and the United Kingdom; consumption amounts are not available. Information of the uses of cobalt are available (Cobalt Development Institute 2000; Donaldson 1986; Hodge 1993; IARC 1991; Richardson 1993; USGS 1998). Cobalt-containing products are mostly used in the workplace, although some consumer products contain cobalt.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The TRI for 1999 became available in May of 2001 (TRI99 2001). Starting in 1998, metal mining, coal mining, electric utilities, and RCRA/solvent recovery industries were required to report to the TRI. These sectors include those contributing greatest environmental releases of cobalt and cobalt compounds, giving us a much more complete picture of cobalt releases to the environment. The TRI also contains information on the on-site and off-site disposal and management of wastes (e.g., recycling, treatment, transfer to POTWs). EPA guidelines address the disposal of hazardous cobalt wastes. The TRI database will be updated yearly and provides a list of industrial production facilities and emissions. The TRI data

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should be used with caution since the 1987 data represent first-time reporting by these facilities. Only certain types of facilities were required to report. This is not an exhaustive list.

Environmental Fate. There are data that permit assessment of the environmental fate and transport of cobalt in water and soil (Section 6.3). Sediment and soil are the ultimate sinks for cobalt. There is a paucity of data in the literature regarding the chemical forms of cobalt released to the atmosphere and their transformations in air. This information would facilitate the determination of the transport and persistence of cobalt in the atmosphere. Additional data elucidating the mode of speciation of cobalt in water and soil would also be desirable. For example, under what circumstances might Co(III) compounds be formed in the environment and how long would they persist?

Bioavailability from Environmental Media. No information was located regarding absorption of cobalt in humans following dermal exposure. Absorption by the inhalation and oral routes in humans has been studied, but the results vary considerably (see Section 3.3.1.1.) (Foster et al. 1989; Harp and Scoular 1952; Sedlet et al. 1958; Sorbie et al. 1971; Valberg et al. 1969). These variations were attributed to differences in the types and doses of cobalt compounds given, to the nutritional status of the subjects following oral exposure, and to particle size differences following inhalation exposure. Additional data assessing the absorption of cobalt following soil ingestion by children may be helpful. Data in animals are plentiful for both inhalation and oral routes and correlate well with the human data (Andre et al. 1989; Bailey et al. 1989; Collier et al. 1989; Kreyling et al. 1986; Patrick et al. 1989; Talbot and Morgan 1989). Data in animals following dermal exposure suggested that cobalt is not absorbed well through intact skin, but is rapidly taken up through damaged skin. Data regarding the bioavailability of cobalt following dermal exposure is important because dermal exposure to cobalt in the workplace is probable.

Food Chain Bioaccumulation. Bioaccumulation in the food chain is important in assessing the human exposure to cobalt from the consumption of food. Data are available that indicate that cobalt is not taken up appreciably by plants and does not biomagnify up the food chain (Baudin and Fritsch 1987; Baudin et al. 1990; Boikat et al. 1985; Francis et al. 1985; Kloke et al. 1984; Lux et al. 1995; Mascanzoni 1989; Mejstrik and Svacha 1988; Mermut et al. 1996; Palko and Yli-Hala 1988; Smith and Carson 1981; Tolle et al. 1983; Watabe et al. 1984).

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Exposure Levels in Environmental Media. Monitoring data on levels of cobalt in air, water, and food permits the estimation of exposure from these sources. Data are available on the cobalt levels in ambient air (Golomb et al. 1997; Hasanen et al. 1990; Schroeder et al. 1987; Smith and Carson 1981; Sweet et al. 1993; Wiersema et al. 1984). However, the data are not sufficiently recent or broad-based for estimating the current levels of exposure to cobalt in the general U.S. population and particularly those living near cobalt-containing hazardous waste sites. In addition, in only isolated studies was there an assessment of the concentration of cobalt associated with coarse and fine particles (Sweet et al. 1993) or an average annual level obtained at a site (Golomb et al. 1997). Similarly, levels of cobalt in ambient water, while generally low, are also not sufficiently broad-based or recent to be satisfactory (Bargagli 2000; Bruce and McMahon 1996; Cassidy et al. 1982; Eckel and Jacob 1988; Flaten 1991; Nojiri et al. 1985; Rossmann and Barres 1988; Smith and Carson 1981). This deficiency may be satisfied when the EPA's improved and updated STORET database comes on line. Cobalt levels in Canadian drinking water are #2.0 mg/L (Meranger et al. 1981). However, U.S. drinking water levels haven't been reported. The levels of cobalt in sediment are available (Bargagli 2000; Coakley et al. 1993; Gibbs 1994; Glooschenko et al. 1981; Knutson et al. 1987; Naidu et al. 1997; Shine et al. 1995; Smith and Carson 1981; Trocine and Trefry 1996; Villanueva and Botello 1998), but more data on levels in soil and in the vicinity of industrial and hazardous waste sites would be useful. Few data on the levels of cobalt in U.S. foods are available, although studies from Canada and Sweden are available that indicate that cobalt levels in food items are generally low (Barceloux 1999; Dabeka and McKenzie 1995; Jorhem and Sundström 1993). In particular, total diet studies of cobalt in U.S. food is lacking. A Canadian total diet study estimated average daily cobalt intake to range from 7 to 15 µg/day for different age-sex groups (Dabeka and McKenzie 1995).

Few data are available on levels of ⁶⁰Co and other cobalt isotopes in environmental media.

Exposure Levels in Humans. The levels of cobalt in hair, nail, and adipose tissues of the general U.S. population are known (EPA 1986; Takagi et al. 1986, 1988). No reliable data on the levels of this substance in blood (or plasma) and urine of the general U.S. population were found, although such data are available for certain European populations including occupationally-exposed groups (Table 6-8). These data may be important for establishing the background exposure level of cobalt. No data on the levels of cobalt in any body tissue or fluid for populations living near hazardous waste sites are available. Such data would be important in assessing the exposure levels of this group of people.

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Exposures of Children. Dabeka (1989) reported the levels of cobalt in various formulas and milk products consumed by children in Canada, and Dabeka and McKenzie (1995) determined the mean dietary intake of Canadian children as young as 1–4 years of age. Nriagru (1992) reported levels of cobalt in human milk from several countries. No analogous U.S. studies were found. Cobalt levels in the tissue and body fluids of children have not been found.

Child health data needs relating to susceptibility are discussed in Section 3.12.2 Identification of Data Needs: Children's Susceptibility.

Exposure Registries. No exposure registries for cobalt were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The compound will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to cobalt and its compounds.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2000) database provides additional information obtainable from a few ongoing studies that may fill in some of the data needs identified in Section 6.8.1. These studies are summarized in Table 6-9.

Remedial investigations and feasibility studies conducted at the NPL sites known to be contaminated with cobalt will add to the available database on exposure levels in environmental media, exposure levels in humans, and exposure registries, and will increase the current knowledge regarding the transport and transformation of cobalt in the environment. No other long-term research studies pertaining to the environmental fate of cobalt or to occupational or general population exposures to cobalt were identified.

Table 6-9. Ongoing Studies on Cobalt

Investigator	Affiliation	Research description	Sponsor
Bates, GT	Alcorn State University, Agriculture, Lorman, Michigan	To develop profiles of selected trace minerals in the Memphis soil and the forage crops grown on this soil and to compare these to those reported in the literature relative to toxicities or deficiencies. To monitor levels of trace minerals in the hair, tissues, and body fluids of beef cattle fed forages produced on the Memphis soil and to compare these levels to those in the soil and forages.	USDA Cooperative State Research Service
Longnecker, Matthew	NIEHS, NIH	Evaluate the use of toenail levels as a measure of exposure by analyzing toenail and whole-diet homogenates by neutron activation analysis. Toenails reflect exposure over a longer period of time than do blood or urine measures, and are less likely to be influenced by contamination than hair.	NIEHS
Moffett, James F	Woods Hole Oceanographic Institution, Woods Hole, Massachusetts	It is known that trace metals in seawater affect ocean phytoplankton and bacteria differently depending upon their concentrations and chemical forms. In addition, such organisms are capable of secreting complexing agents that change trace metal speciation, making them more or less assimilable and more or less toxic. This phenomena will be studied as a two-way street: water column cobalt affecting oceanic microbial communities and oceanic microbial communities affecting the water column cobalt chemistry. The studies will involve field (Sargasso Sea) and laboratory studies with two species of cyanobacteria and their biogeochemical relationship.	NSF, Division of Ocean Sciences
Odom, JW	Auburn University, Agronomy and Soils Department	The occurrence, measurement, and mapping of plant micronutrients and trace elements, including cobalt, in Alabama soils will be determined including both total and extractable forms of these elements in selected soil profiles.	USDA Cooperative State Research Service
Perry, DL	Lawrence Berkeley Laboratory, University of California	One of the most important mechanisms that affects toxic metal subsurface transport is that of organic complexation. The research will involve first the synthesis of organic-metal ion complexes involving cobalt, uranium, and chromium with the multidentate chelating carboxylic acids diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), and cyclohexanediaminetetraacetic acid (CDTA). Auger, X-ray photoelectron, FT-IR, and Raman spectroscopies will then be used to study the chemistry and spectroscopy of the mixed contaminants and devise new analytical approaches for the detection of the mixed contaminants in soil and groundwater. The data derived from this research will provide an extremely critical experimental chemical base to model hydrologic transport of cocontaminant organic-metal ion species in subsoils and groundwater.	USDOE Energy Research

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Table 6-9. Ongoing Studies on Cobalt (*continued*)

Investigator	Affiliation	Research description	Sponsor
Stone, AT	Johns Hopkins University, Baltimore, Maryland	This project is concerned with the mobilization of MnO ₂ and FeOOH-bound toxic metals in subsurface arising from an influx of natural organic matter or organics-containing wastes. Work is reported that examines how reductant, complexant, and adsorptive characteristics of constituent organic chemicals affect the oxidation state and solid-solution partitioning of cobalt, nickel, copper, and lead. In this work, representative low-molecular weight organic compounds and natural organic matter (NOM)-containing subsurface samples are added to hydrous oxide suspensions containing toxic metals such as cobalt, lead, mercury, and uranium. Changes in toxic metal oxidation state, solubility, and speciation are explored in relation to the complexant, reductant, and adsorptive characteristics of the added organic constituents. The goal of this work is to improve the ability to predict toxic metal speciation and the potential for migration at contaminated subsurface sites.	USDOE Energy Research
Tyler, J	University of Missouri, Columbia, Missouri	To survey the prevalence and geographic distribution of selenium, copper, zinc and cobalt deficiency in Missouri feeder calves. Blood will be analyzed.	USDA Cooperative State Research Service
Zachara, JM	Pacific Northwest Laboratory, Richland, Washington	To investigate interfacial geochemical reactions of subsurface materials to chemical mixtures in order to improve reaction-based models of sorption and abiotic degradation used to predict contaminant concentrations in subsurface environments. The scientific focus is on multispecies interactions between organic substances and inorganic contaminants (e.g., metals, radionuclides) such as competitive sorption, cosorption, and cosolution. Organic substances (humic materials, organic acid complexing agents, and organic solvents) and metals-radionuclides (U, Co, Pb, Cs, Sr, and Tc) representative of chemical constituents on DOE lands are used in carefully selected mixtures to test surface chemical hypotheses about multispecies interactions. Laboratory experimentation involves the contact of these mixtures with (1) subsurface materials having diverse mineral and chemical properties, (2) natural clays, oxides, and organic matter isolated from subsurface sediments, and (3) reference mineral-organic surfaces. Various instrumental techniques employed to investigate the nature of the multispecies surface reactions include laser microelectrophoresis, luminescence spectroscopy, and calorimetry. Multispecies, multisite surface complexation models, are employed to evaluate hypotheses regarding dominant surface reaction mechanisms, reactive contributions of different sorbents, and the effects of different cocontaminant interactions.	USDOE Energy Research

NIEHS = National Institute of Environmental Health Sciences; NIH = National Institute of Health; NSF = National Science Foundation USDA = U.S. Department of Agriculture; USDOE = U.S. Department of Energy